Use of ICP-MS in analysing radioisotopes

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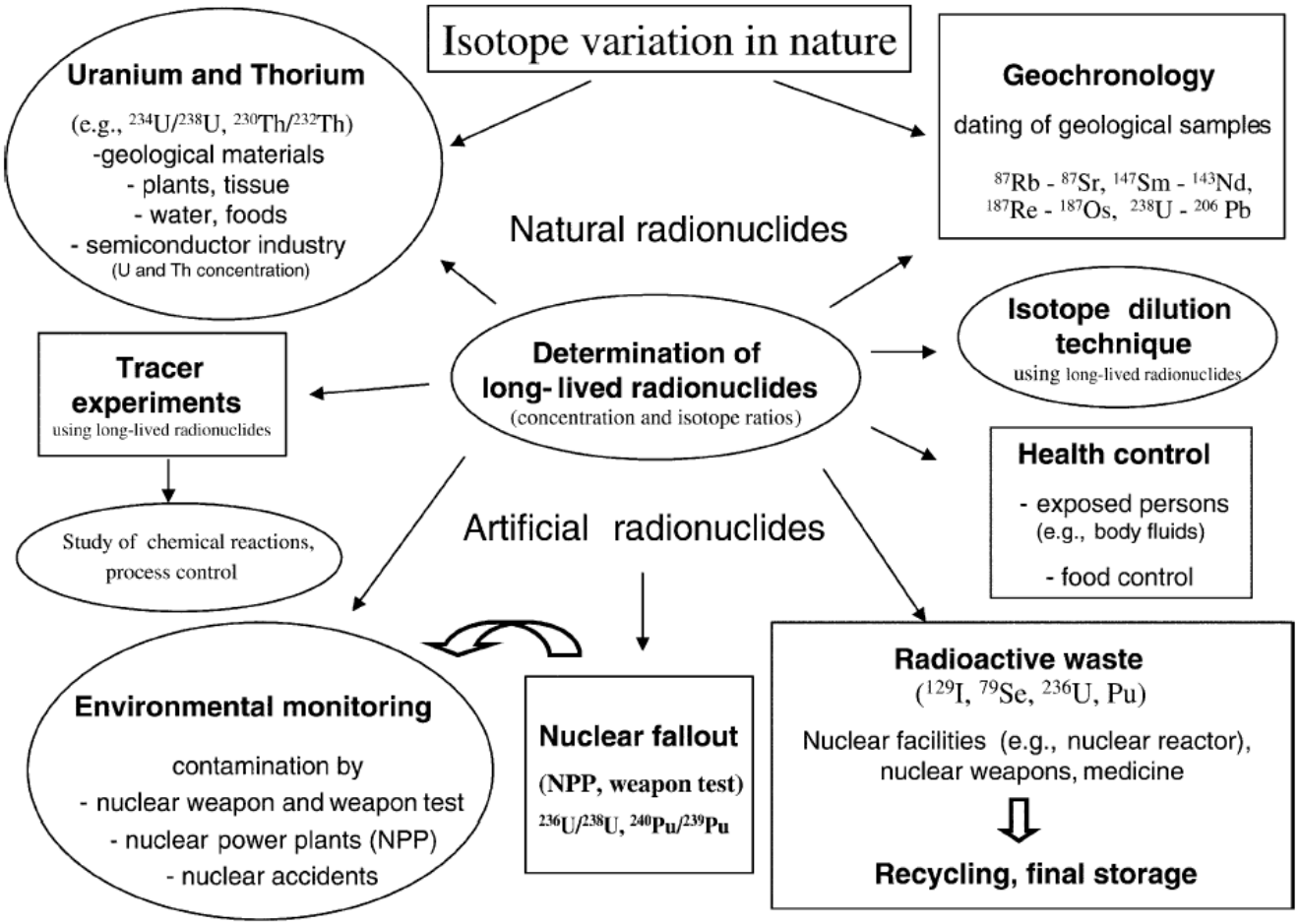
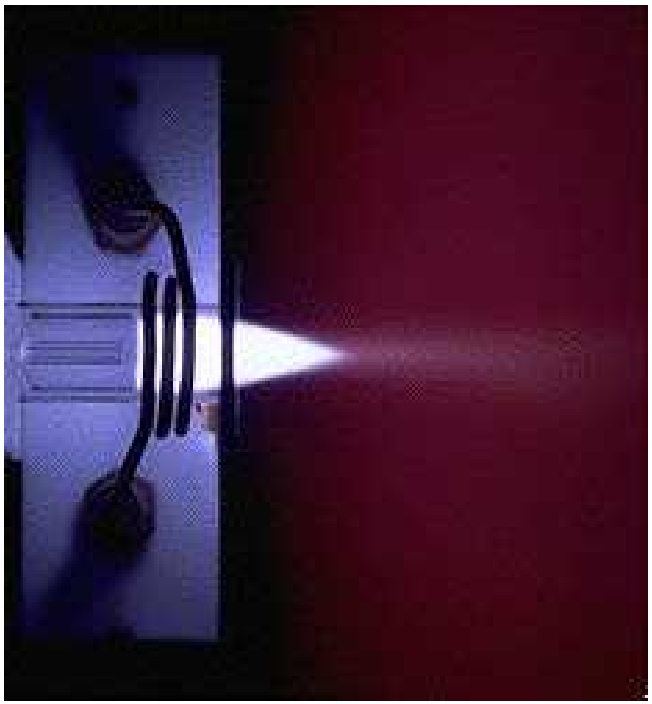


Fig. 1. Overview of application fields for determination of long-lived radionuclides.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)



History

- ICP-AES in 1960'ies
- Plasma & MS merging in 1974 using a DC-plasma, Surrey UK.
  (A.L. Gray, A plasma source for mass analysis, *Proc. Soc. Anal. Chem*, 11, 182-183).
- ICP & MS merging in 1980, Ames Lab, USA
  (R.S. Houk et.al., Inductively coupled argon plasma as an ion source for mass spectrometric determination of trace elements. *Anal. Chem*, 52, 2283-2289.).
- Microwave plasma – MS, Toronto Canada.
  (D.J. Douglas & J.B. French, Elemental analysis with a microwave induced plasma quadrupole mass spectrometer system. *Anal. Chem*. 53, 37-41.)
- First commercial instruments in 1983.
  PlasmaQuad by VG Isotopes, "UK-system"
  Elan by Sciex, "Canada system"

Inductively Coupled Plasma

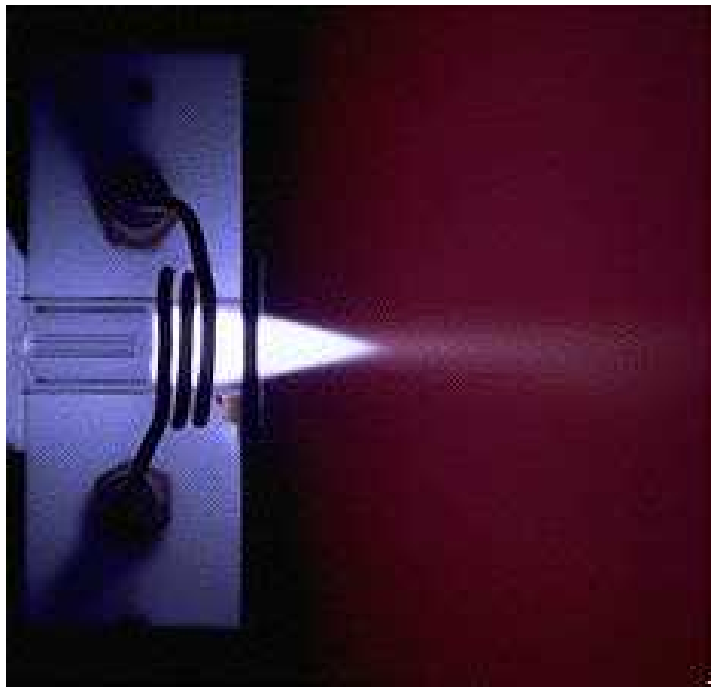
- Electrodeless discharge formed in a flowing gas stream enclosed in a quartz torch. Sustained by the induction of electrical energy using a coil around the torch. Atmospheric pressure!

- ”Plasma”: Langemuir in 1928 adopted the word to describe a discharge through a gas confined at low pressure.

- ”Any volume of an ionized gas where the total charge is zero”

Lightning the plasma

- Seed electrons to the flowing gas (piezoelectric spark)
- Apply a high-frequency electromagnetic field (20-50 MHz)
- Electrons will be accelerated back- and forwards in oscillating RF-field
- Multiplication of free electrons – plasma reached in a few milliseconds.



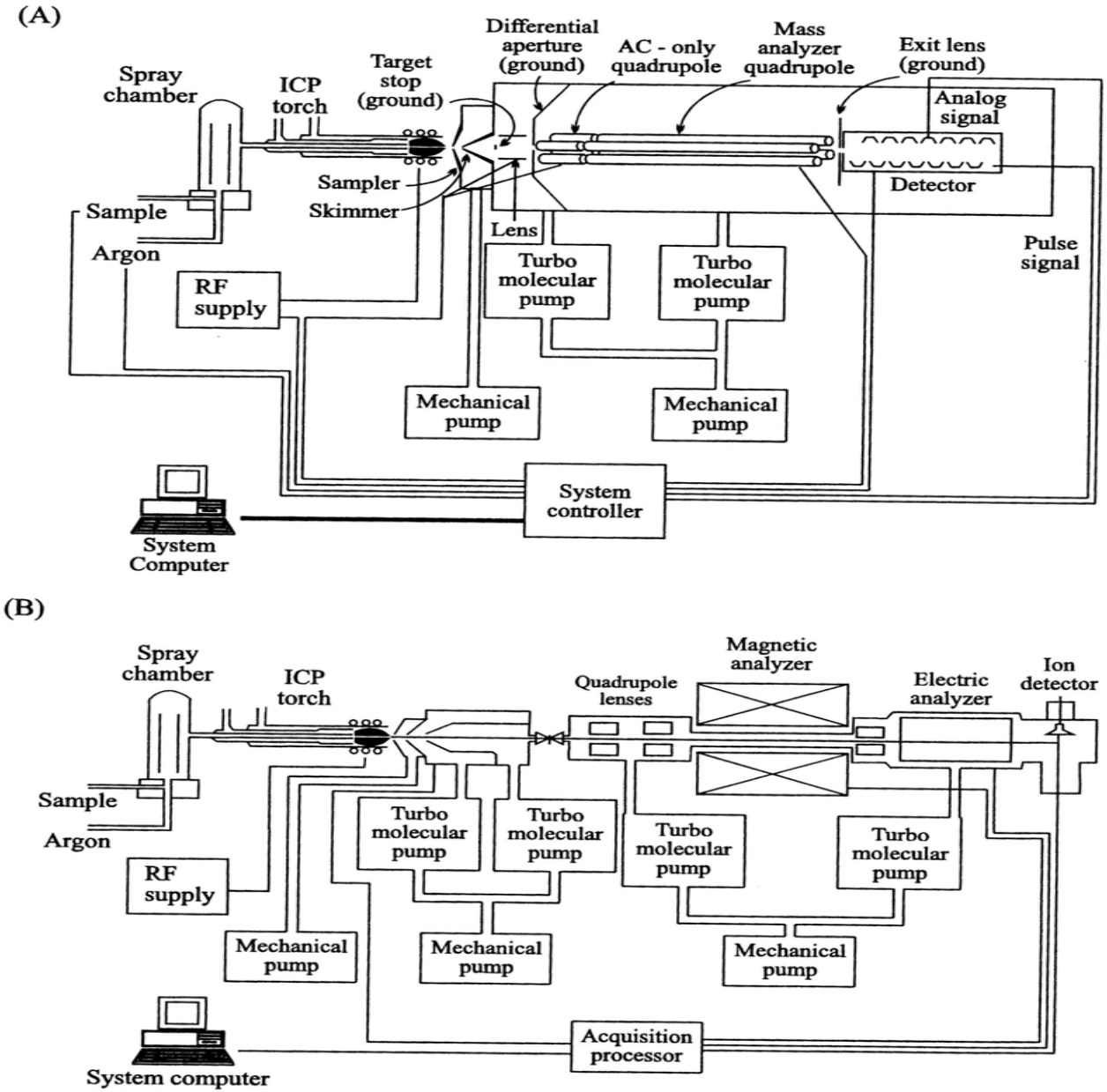


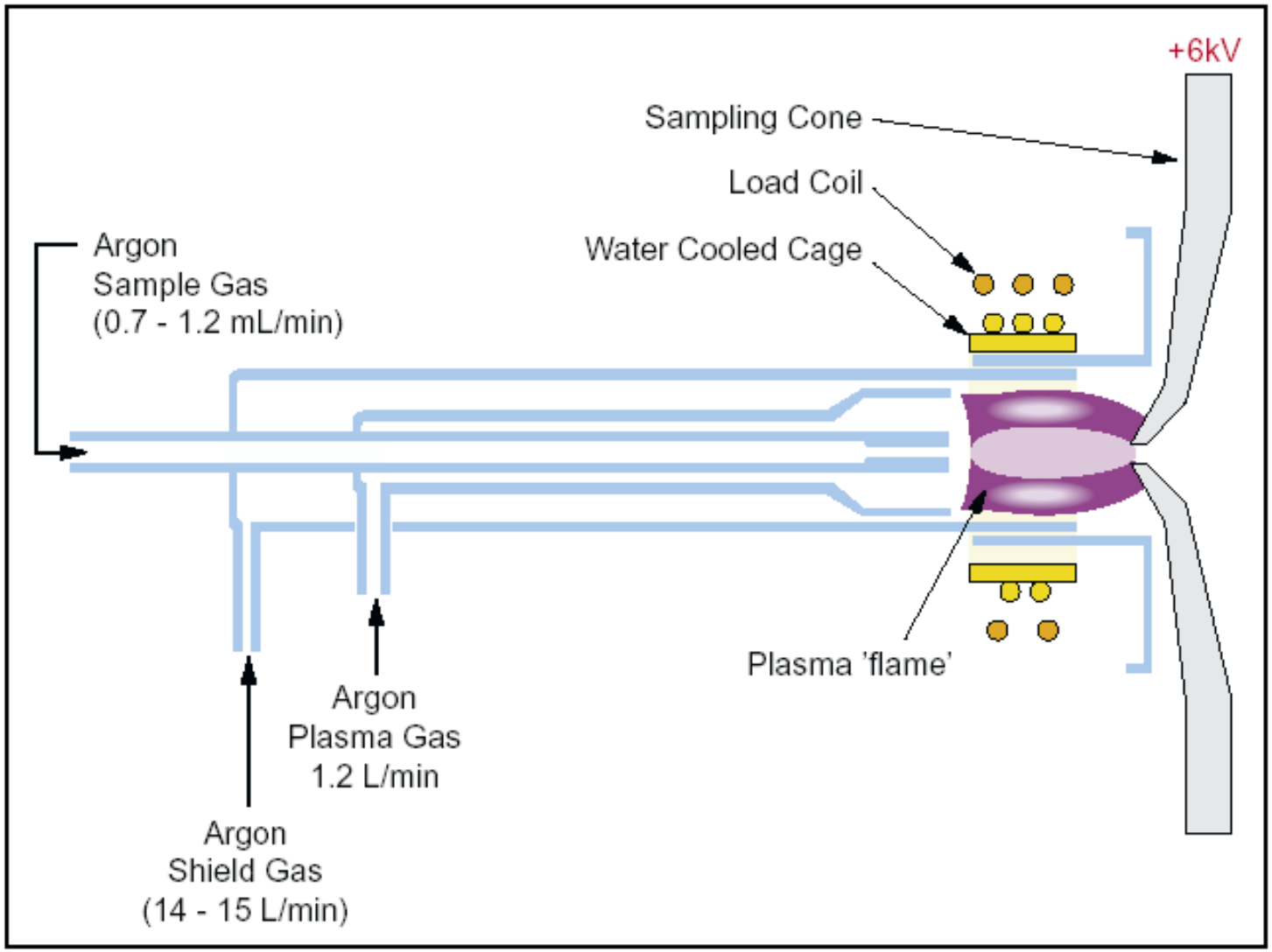
Figure 1.4 (A) Schematic diagram of a quadrupole ICPMS, the Elan 6000. (Courtesy of the Perkin-Elmer/Sciex Corporation.) (B) Schematic diagram of a magnetic sector ICPMS, the JMS-PLASMAX2. (Courtesy of JOEL Incorporated.)

Risø ICP-MS instruments

Thermo X-series II
Quadrupole ICP-MS

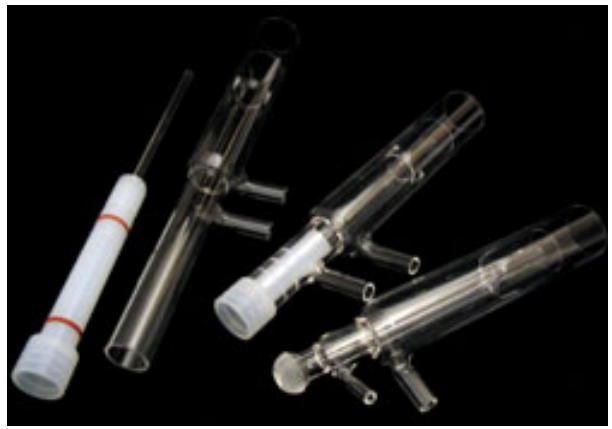
Plasma Trace 2
Sector field ICP-MS

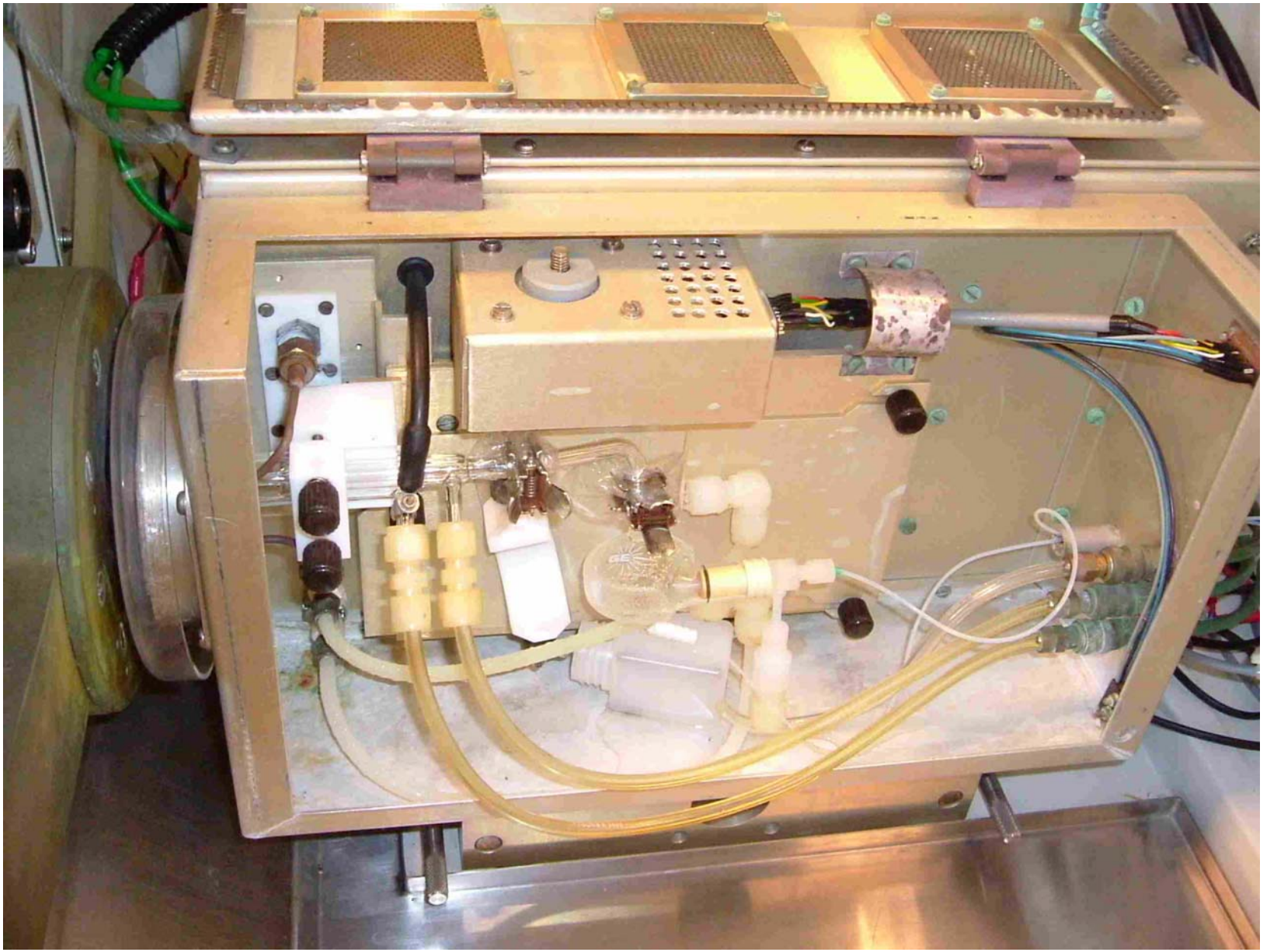
Torch, loadcoil and interface

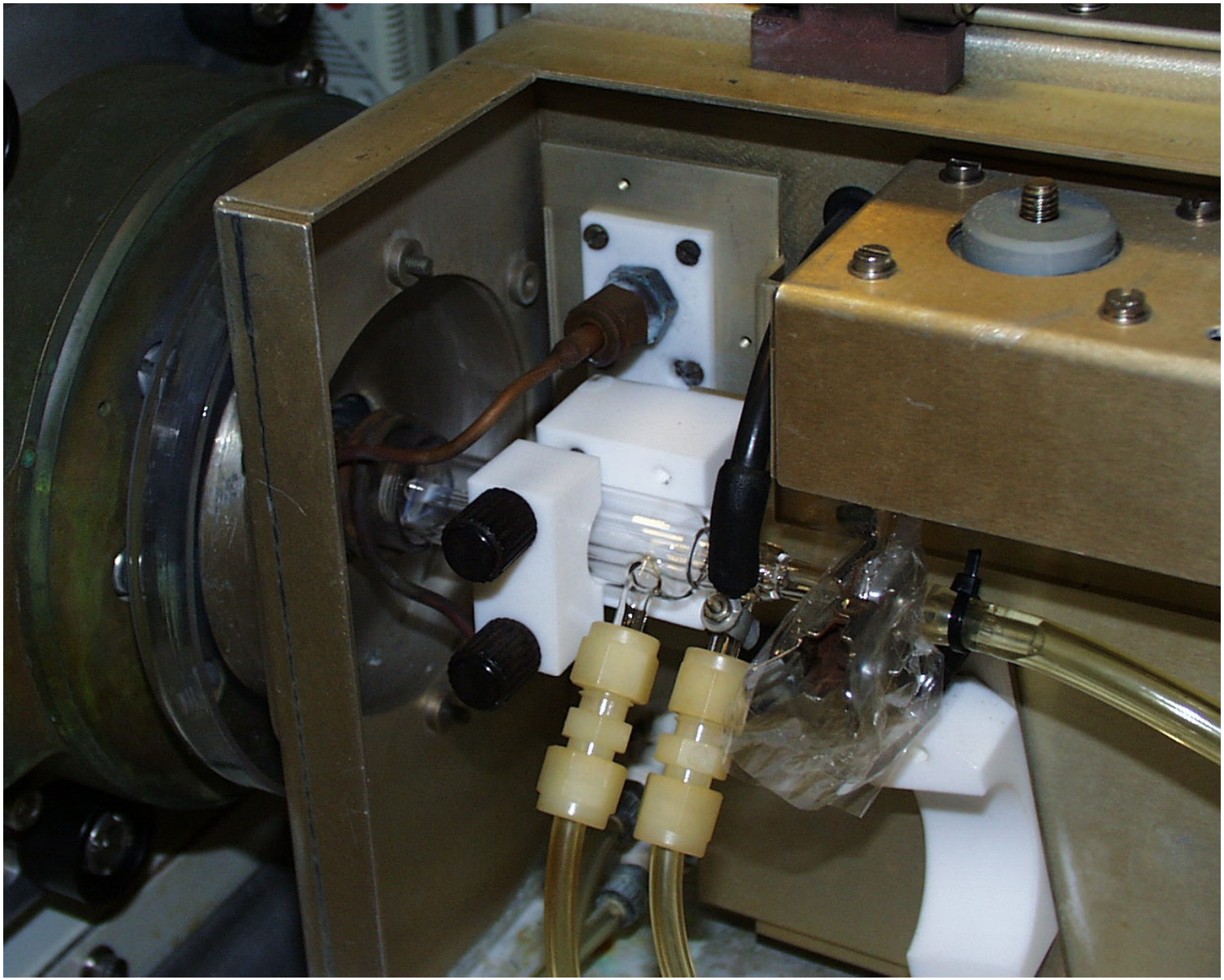


Torch & load coil

- Three concentric coaxial glass/quarts tubes
- Outer tube: About 25mm longer than the two others.
- Cool gas: Rotating 12-16 L min^{-1}
- ”Auxiliary” gas tube (plasma gas): 0.6-1.4 L min^{-1}
- Injector or nebuliser gas: 0.5-1 L min^{-1}
- Induction coil (load coil);
- Water cooled
- Copper
- Part of the oscillatory circuit called the RF-generator.
- 20-40 MHz
- Power output 1-2.5 kW.







The plasma – ms interface

- Sampling and skimming process
- In early days only sampler- 0.05mm
- Sample orfice must be large enough to sample centre of plasma while at the same time small enough not to disturb the plasma.

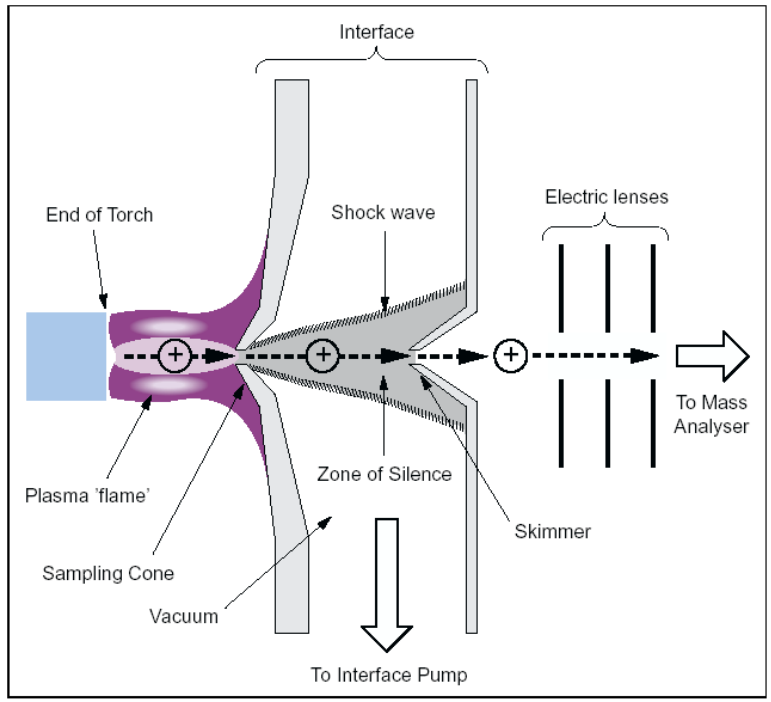


Table 1.3 Distribution of ionization energies among the elements for singly and doubly charged ions. Grouped in steps of 1 eV.

Ionization Energy (eV)	Elements	
< 7	Li, Na, Al, K, Ca, Sc, Ti, V, Cr, Ga, Rb, Sr, Y, Zr, Nb, In, Cs, Ba, La, Ce, Pr, Nd, Pm Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Tl, Ra, Ac, Th, U	
7–8	Mg, Mn, Fe, Co, Ni, Cu, Ge, Mo, Tc, Ru, Rh, Ag, Sn, Sb, Ta, W, Re, Pb, Bi	
8–9	B, Si, Pd, Cd, Os, Ir, Pt, Po	
9–10	Be, Zn, As, Se, Te, Au	2^+ *Ions*
10–11	P, S, I, Hg, Rn	Ba, Ce, Pr, Nd, Ra
11–12	C, Br	Ca, Sr, La, Sm, Eu, Tb, Dy, Ho, Er
12–13	Xe	Sc, Y, Gd, Tm, Yb, Th, U, Ac
13–14	H, O, Cl, Kr	Ti, Zr, Lu
14–15	N	V, Nb, Hf
15–16	Ar	Mg, Mn, Ge, Pb
> 16	He, F, Ne	All other elements

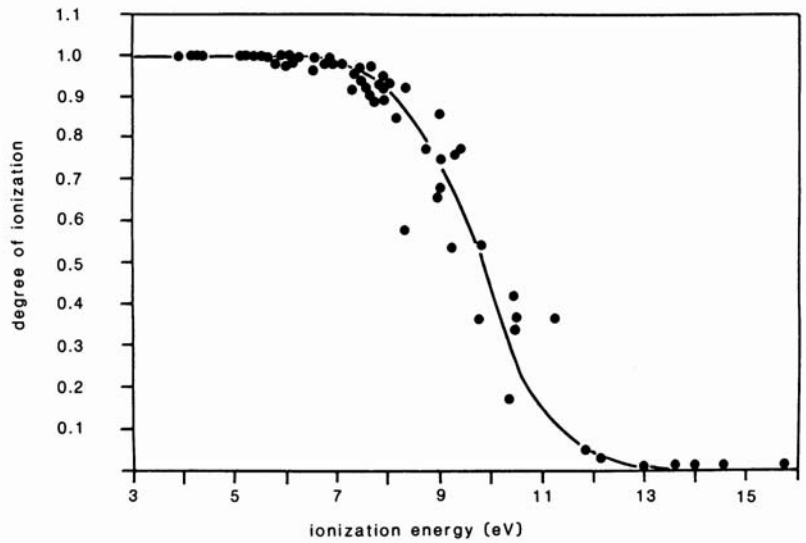


Figure 1.7 Degree of ionization α versus ionization energy for singly charged ions in the ICP. Calculated for a representative selection of 59 elements from the Saha equation, assuming values of T_i of 8000 K and n_e of $2.5 \times 10^{15}\,cm^{-3}$.

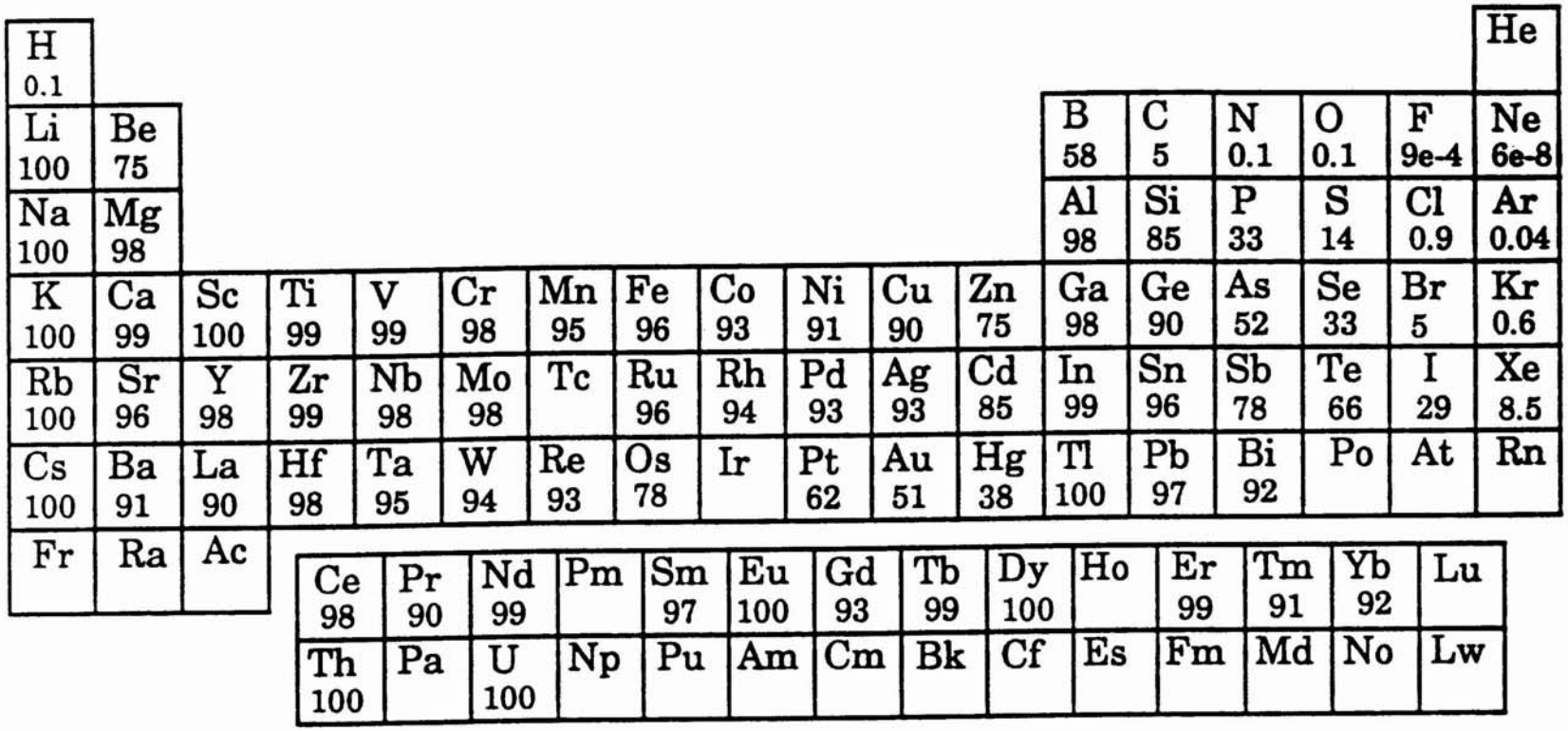


Figure 8.1 Calculated degrees of ionization, $[M^+]/([M^+] + [M])$, expressed as percentages. An ionization temperature of 7500 K and electron number density of 1×10^{15} cm^{-3} were used. (From Reference 10, with permission.)

Table 7
Detection limits for actinides in high-purity water by double focusing sector fields ICP-MS

Nuclide	Half life [years]	"ELEMENT" [129] [pg L^{-1}]	"ELEMENT" [129] [kBq L^{-1}]	"Plasma Trace" [175] [pg L^{-1}]
^{230}Th	7.5×10^{4}	0.08	6.2×10^{-8}	20
^{232}Th	1.4×10^{10}	0.1	4.1×10^{-13}	
^{233}U	1.6×10^{5}	0.07	2.5×10^{-8}	
^{238}U	4.5×10^{9}	0.2	2.4×10^{-12}	20
^{237}Np	2.1×10^{16}	0.05	1.3×10^{-9}	2
^{239}Pu	2.4×10^{4}	0.04	9.4×10^{-8}	5
^{243}Am	7.9×10^{3}	0.05	3.6×10^{-7}	

Table 9.15 The detection limits (DL) obtained using magnetic sector-ICP-MS with ultrasonic nebuliser

Nuclide	Half-life (years)	CPS per pg g^{-1}	DL (fg g^{-1})	DL (Bq g^{-1})
^{99}Tc	2.14×10^{5}	2.28×10^{2}	2.6	1.60×10^{-6}
^{226}Ra	1.60×10^{3}	1.01×10^{4}	0.1	3.70×10^{-6}
^{232}Th	1.41×10^{10}	7.78×10^{3}	0.2	8.00×10^{-13}
^{237}Np	2.14×10^{6}	5.83×10^{3}	0.2	5.20×10^{-9}
^{238}U	4.47×10^{10}	8.02×10^{3}	0.2	2.40×10^{-12}
^{239}Pu	2.41×10^{4}	6.21×10^{3}	0.2	4.28×10^{-7}
^{240}Pu	6.56×10^{3}	6.21×10^{3}	0.2	1.57×10^{-6}
^{243}Am	7.37×10^{3}	6.56×10^{3}	0.2	1.40×10^{-6}

Table 5. Application of ICP-MS in trace and isotope analysis of long-lived radionuclides in nuclear and environmental materials, radioactive waste and medical samples

Samples	Method	Radionuclides	Detection limits/isotope ratio	References
Fission product solution	ETV-ICP-MS	^{79}Se	13 ng/l	Compte et al. [72]
Thermal water	ICP-QMS + USN (PlasmaQuad PQ2) extraction, ion exchange	^{226}Ra	2 fg/g	Joannon and Pin [69]
Mineral water	ICP-SFMS after separation	^{226}Ra	2 fg/g	Zoriy et al. [73]
Radioactive waste solution	ICP-SFMS ELEMENT, (USN)	^{226}Ra, ^{230}Th, ^{233}U, ^{237}Np, ^{239}Pu, ^{241}Am	0.05 pg/l(^{241}Am) 0.04 pg/l (^{239}Pu) ^{236}U/^{238}U $\sim$ 0.02 (flow injection)	Becker and Dietze [7]
Radioactive waste solution	ICP-SFMS ELEMENT, (DIHEN)	^{226}Ra, ^{230}Th, ^{230}Th, ^{233}U, ^{237}Np, ^{238}U, ^{241}Am	0.1 pg/l(^{241}Am) 0.l pg/l(^{237}Np) ^{236}U/^{238}U $\sim$ 0.00002−0.0001	McLean et al. [30]
Urine	ICP-SFMS (ELEMENT) after separation (1 l urine)	^{239}Pu, ^{240}Pu	1 fg/l ^{240}Pu/^{239}Pu $\sim$ 0.14 (synth. sample)	Zoriy et al. [54]
Urine	ICP-SFMS (ELEMENT) ICP-CC-MS (Platform)	^{90}Sr	0.4 pg/l (ELEMENT) 2 ng/l (Platform)	Vonderheide et al. [53]
Ground water	ICP-SFMS (ELEMENT)	^{90}Sr, ^{239}Pu, ^{240}Pu	11 pg/l (^{90}Sr); 0.1 pg/l (Pu); ^{240}Pu/^{239}Pu $\sim$ 0.17	Zoriy [71]
Sea water	ICP-SFMS (ELEMENT)	^{239}Pu, ^{240}Pu	≈0.1 fg/l (ELEMENT) ≈0.01 fg/l (NuPlasma) ^{240}Pu/^{239}Pu $\sim$ 0.17	Becker et al. [52]

Radioisotopes – in general focus on:

- Sensitivity (transmission of ions to detector)
- Polyatomic interferences
- Abundance sensitivity
- Stability (isotope ratios)

Improving sensitivity

- Matrix removal from sample (separation chemistry)
- High efficiency sample introduction systems
- Instrument optimisation

Pu-analysis at sub-mBq to μBq levels

- Instrument background.
- Procedure blank (Pu)
- Contribution from tracer.
- Memory effects.
- Polyatomic species (including the UH+)
- Abundance sensitivity.

Transport efficiency

- 1 mBq ml^{-1} of ^{242}Pu ($1.7 \cdot 10^{10}$ atoms ml^{-1})
- With USN and 0.4 ml min^{-1} uptake rate produces a count rate of about 10 000 cps.

- $\Rightarrow$ **1 atom per 12 500 detected !**

Efficiency alpha vs. ICP-MS

- **Alpha**: Geometric efficiency about 25%
- **ICP-MS**: Efficiency about 1: 10 000

- **Alpha counting** of ^{239}Pu (24 400 y). Two months counting $\Rightarrow$ about 10^{-6} of sample atoms have decayed (for ^{238}U about 10^{-12}).
- **ICP-MS** measurement of ^{239}Pu takes about 10 minutes. 10^{-4} of sample atoms are detected.

Ways to improve sensitivity

Shielded torch

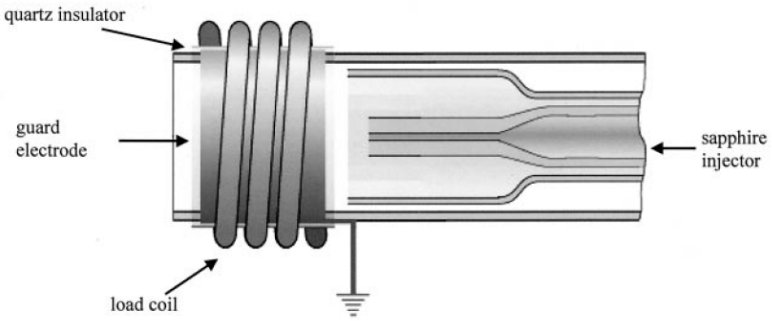


Fig. 15. Plasma shielded torch (GE—guard electrode, courtesy of Finnigan MAT).

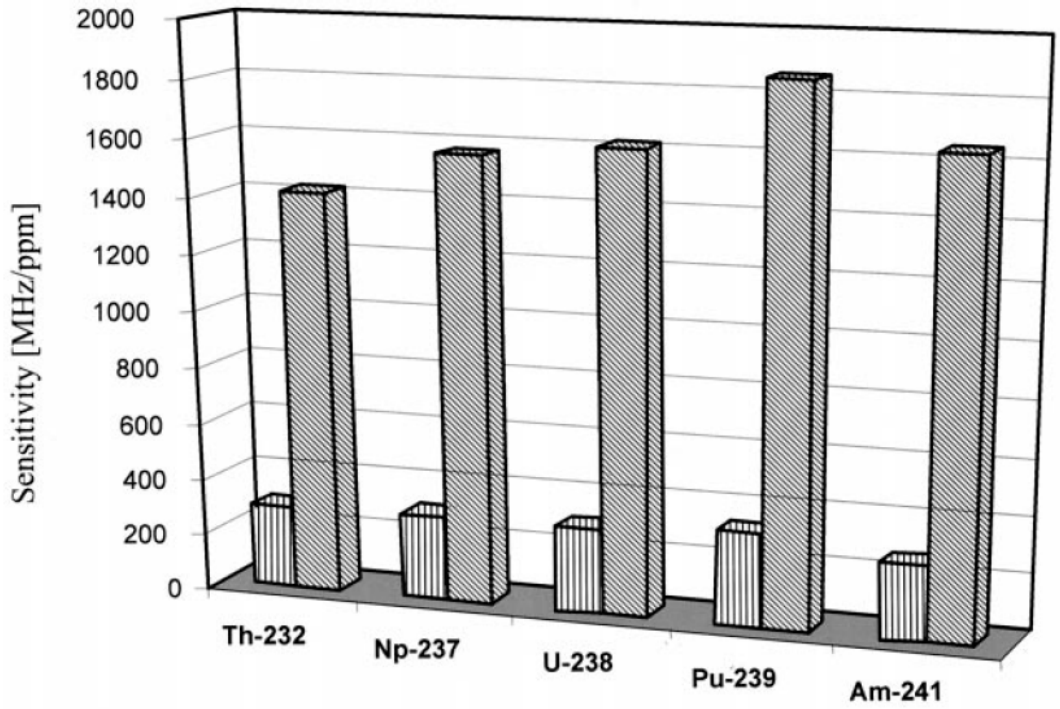
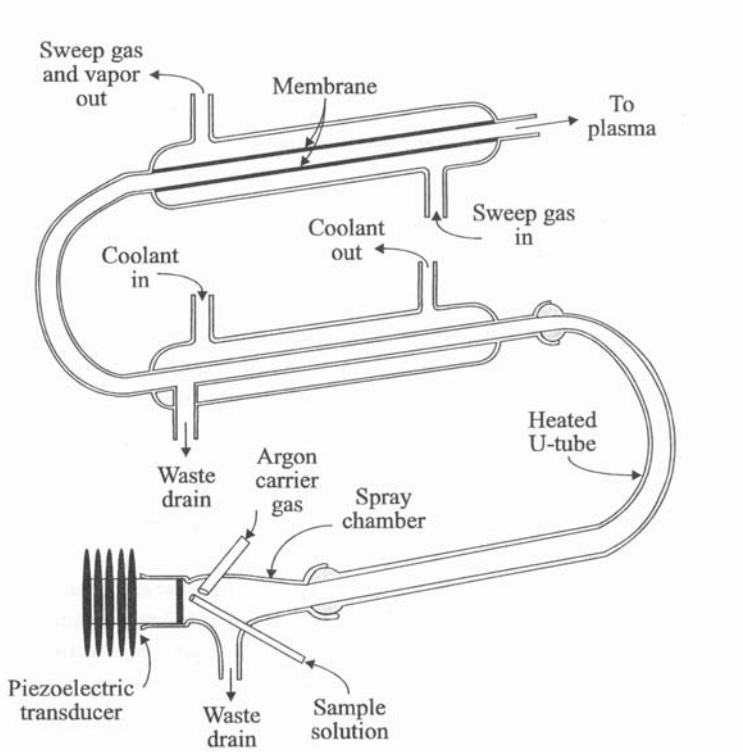
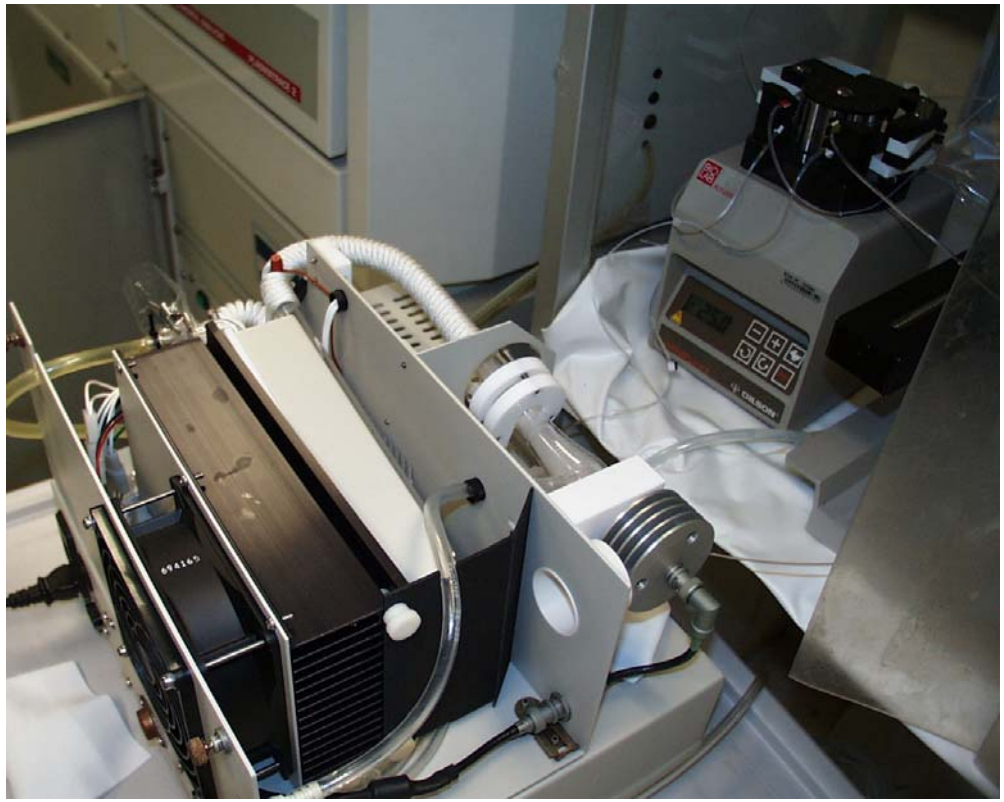


Fig. 16. Comparison of sensitivity of long-lived radionuclides in DF-ICP-MS with and without shielded torch. (diagonal lines, with shielded torch, vertical lines, without shielded torch).

High efficiency nebulisers

(B)



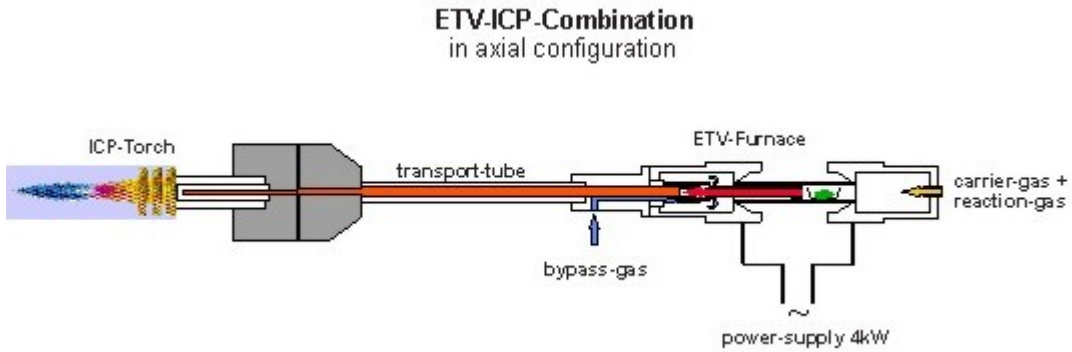


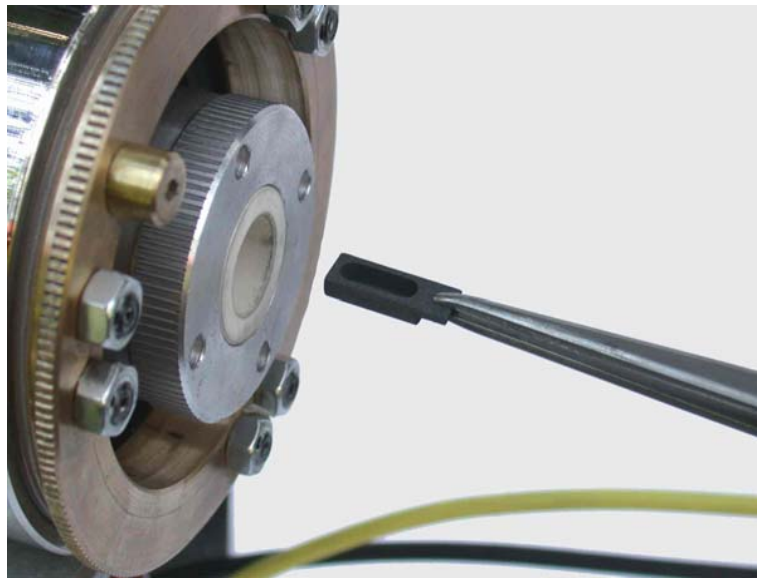
Sensitivity & sample introduction system

	Concentric nebuliser + chilled cyclonic spraychamber	USN
cps per pg s^{-1} to plasma (uranium)	$1.2*10^6$	$1.1*10^8$

Electrothermal vaporization (ETV)

…….also for speciation studies





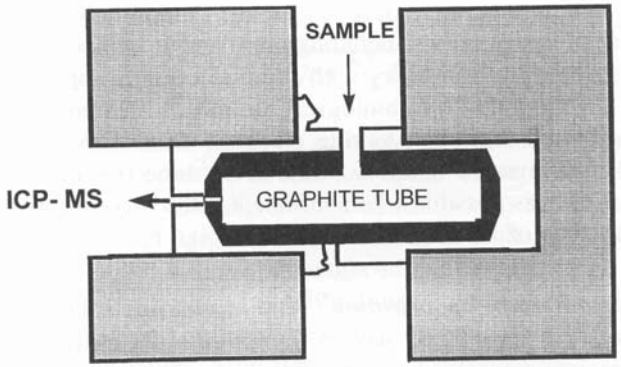
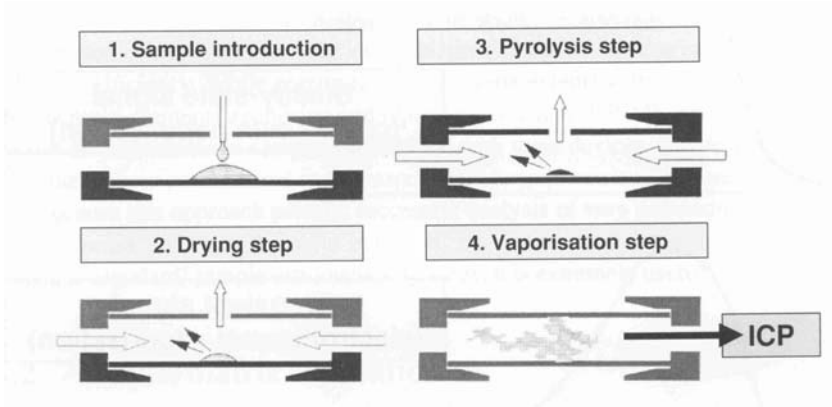


Figure 9.7 Diagram of graphite tube ETV-ICPMS atomizer.



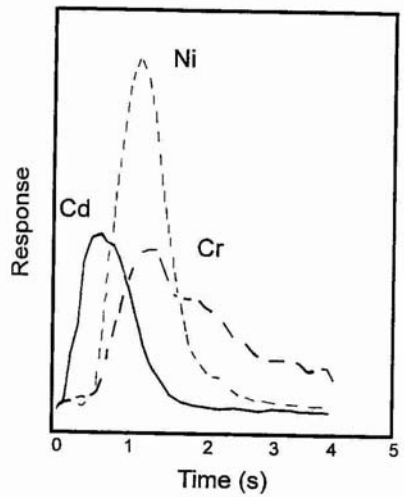
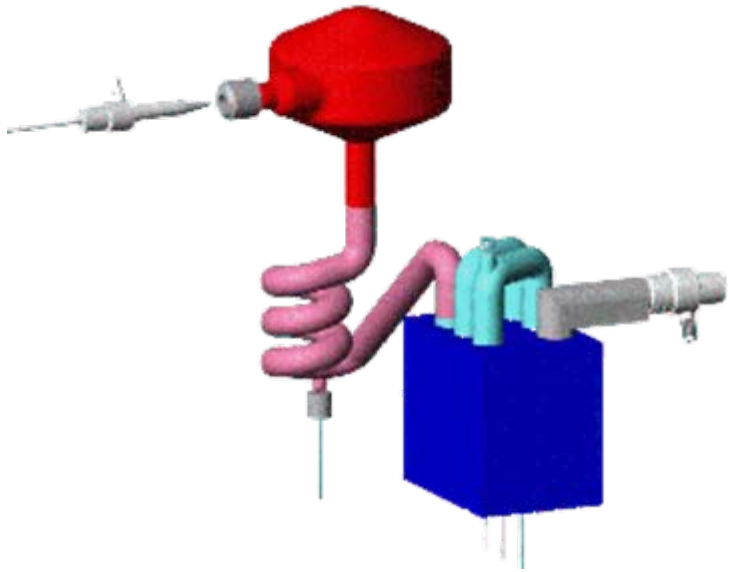
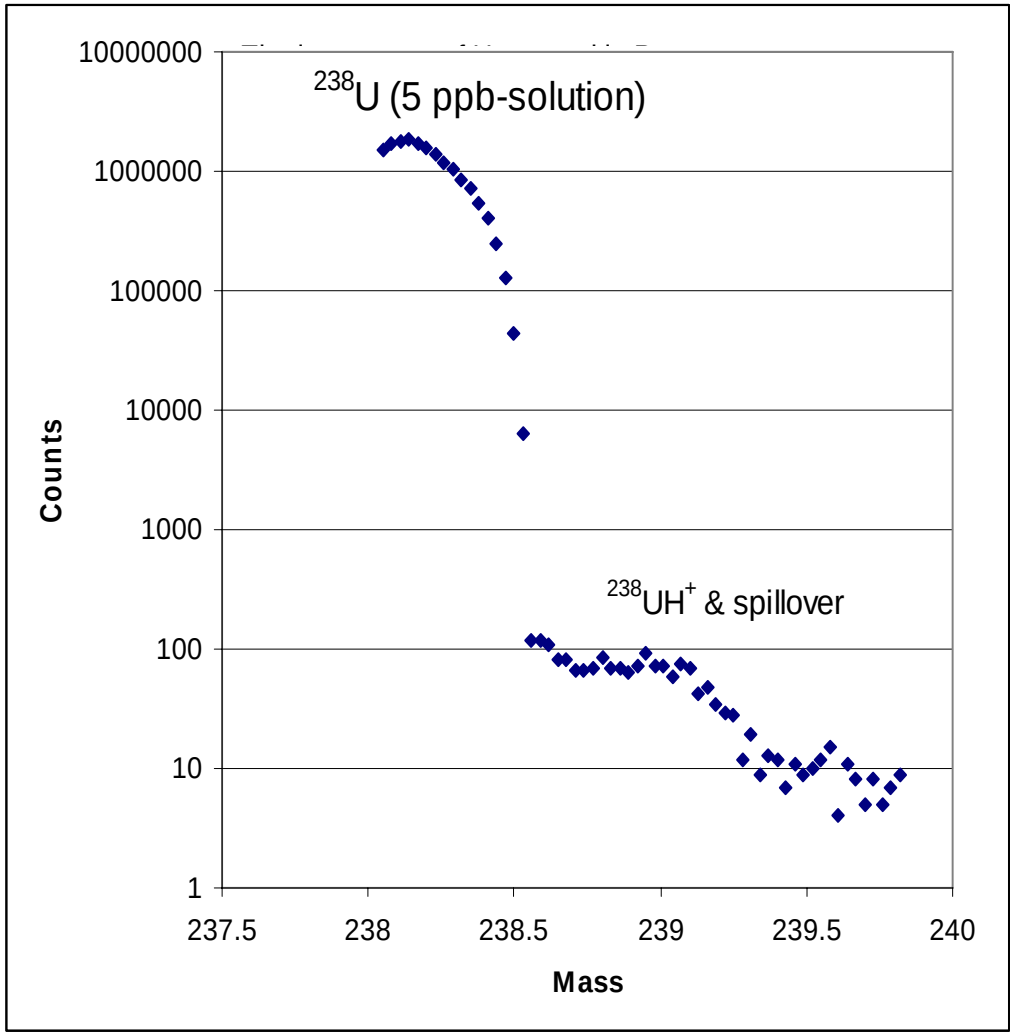


Figure 9.8 Signal responses for typical analytes by ETV-ICPMS. (From Reference 91, with permission.)

….APEX-system



The importance of removing uranium in Pu-measurements (hydride generation and spillover)



The UH+ and ways to minimize it

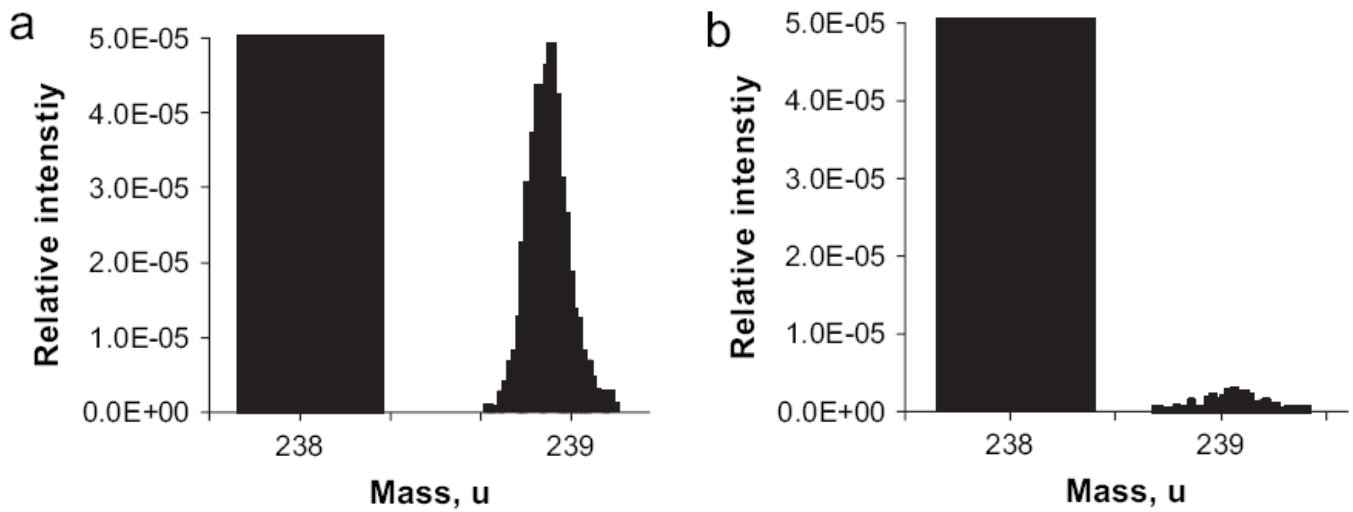


Fig. 2. Uranium hydride ion production in ICP-MS using PFA 100 nebulizer (a) without and (b) with the APEX system.

UH^+/U

Wet plasma (Cyclonic spraychamber)	Dry plasma (USN)
63 ppm	23 ppm

Hydrides important to minimize for ^{236}U analysis.

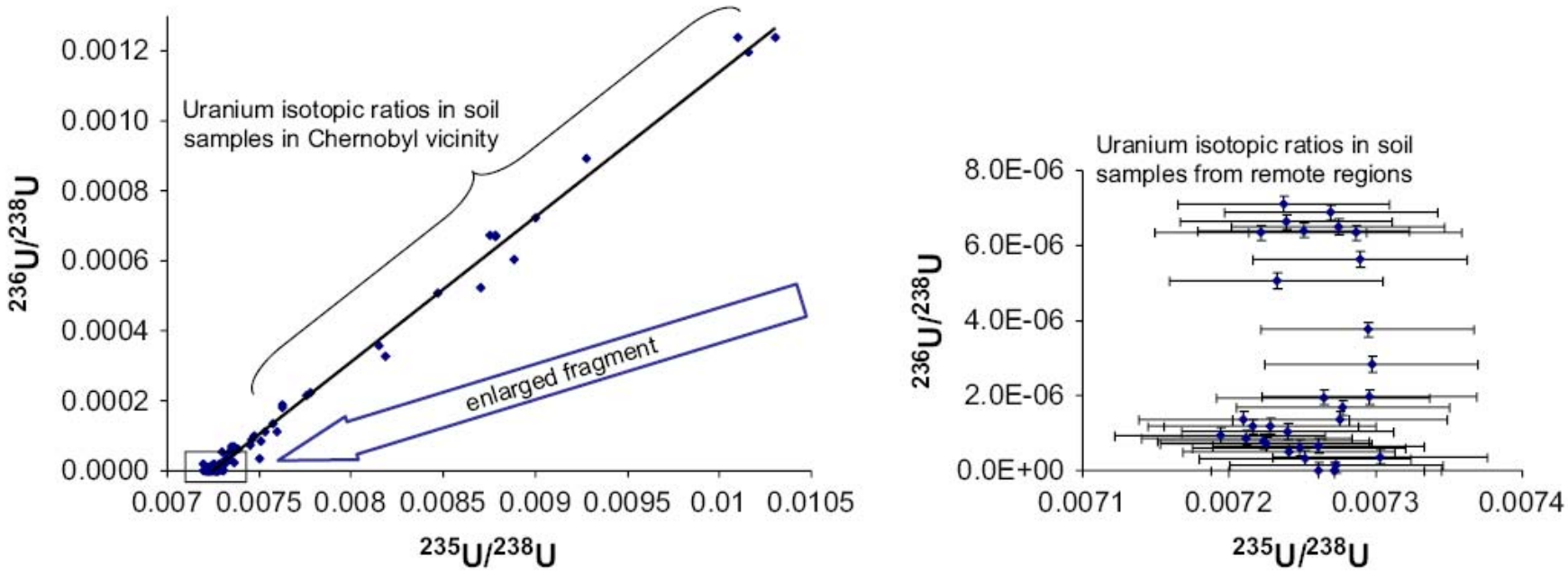


Fig. 4. $^{236}U/^{238}U$ vs. $^{235}U/^{238}U$ ratios in soil samples collected in different regions of Belarus.

Direct Injection High Efficiency Nebuliser (DIHEN)

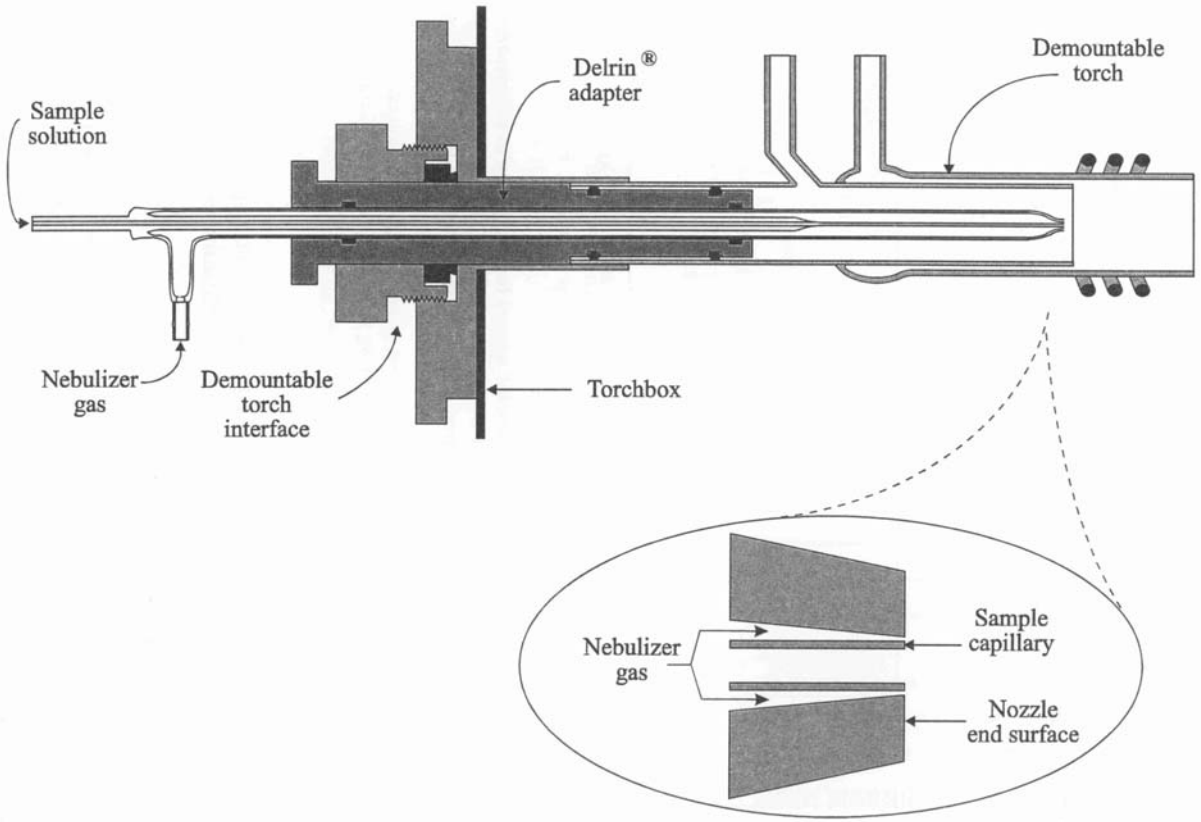
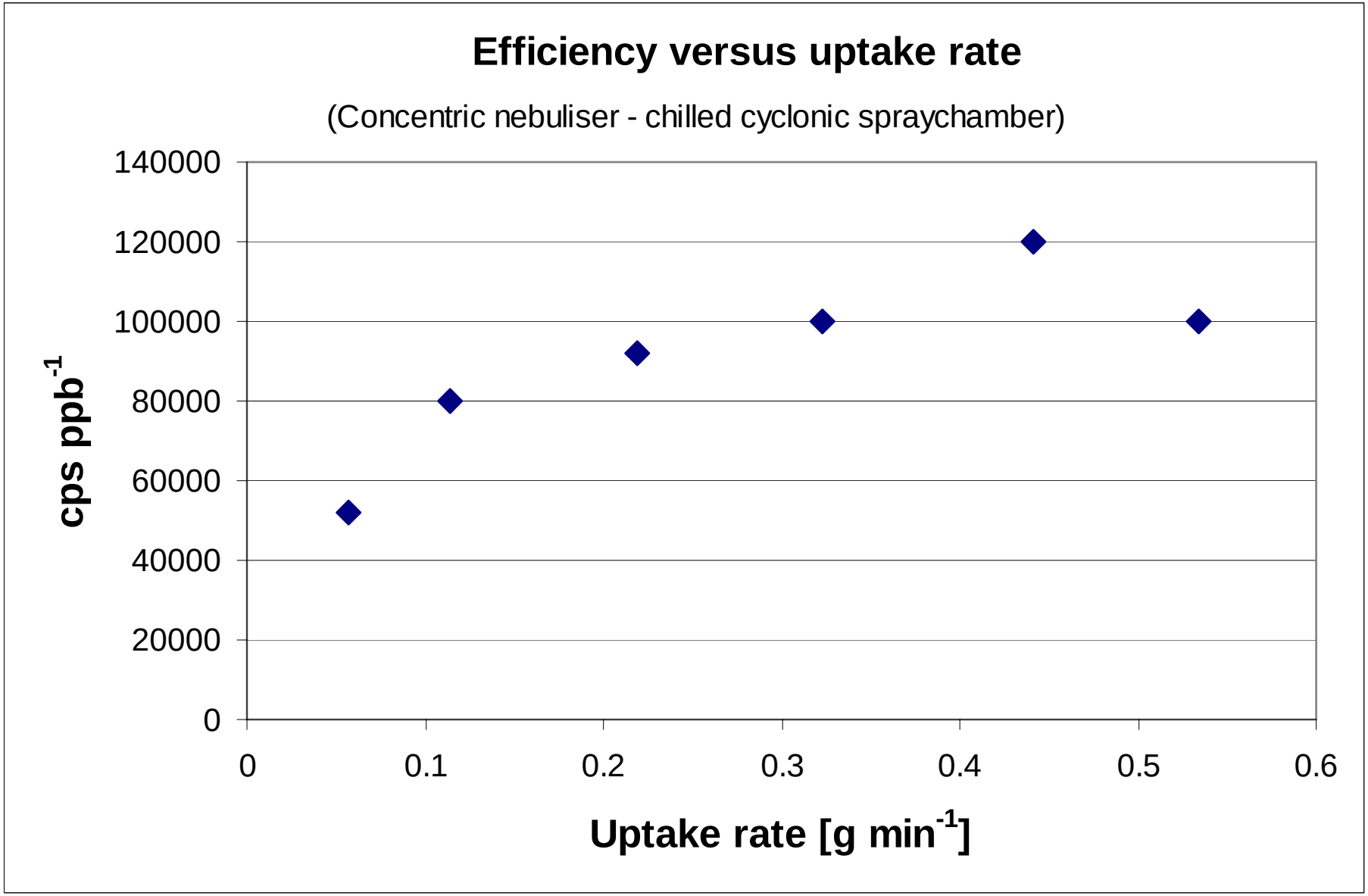
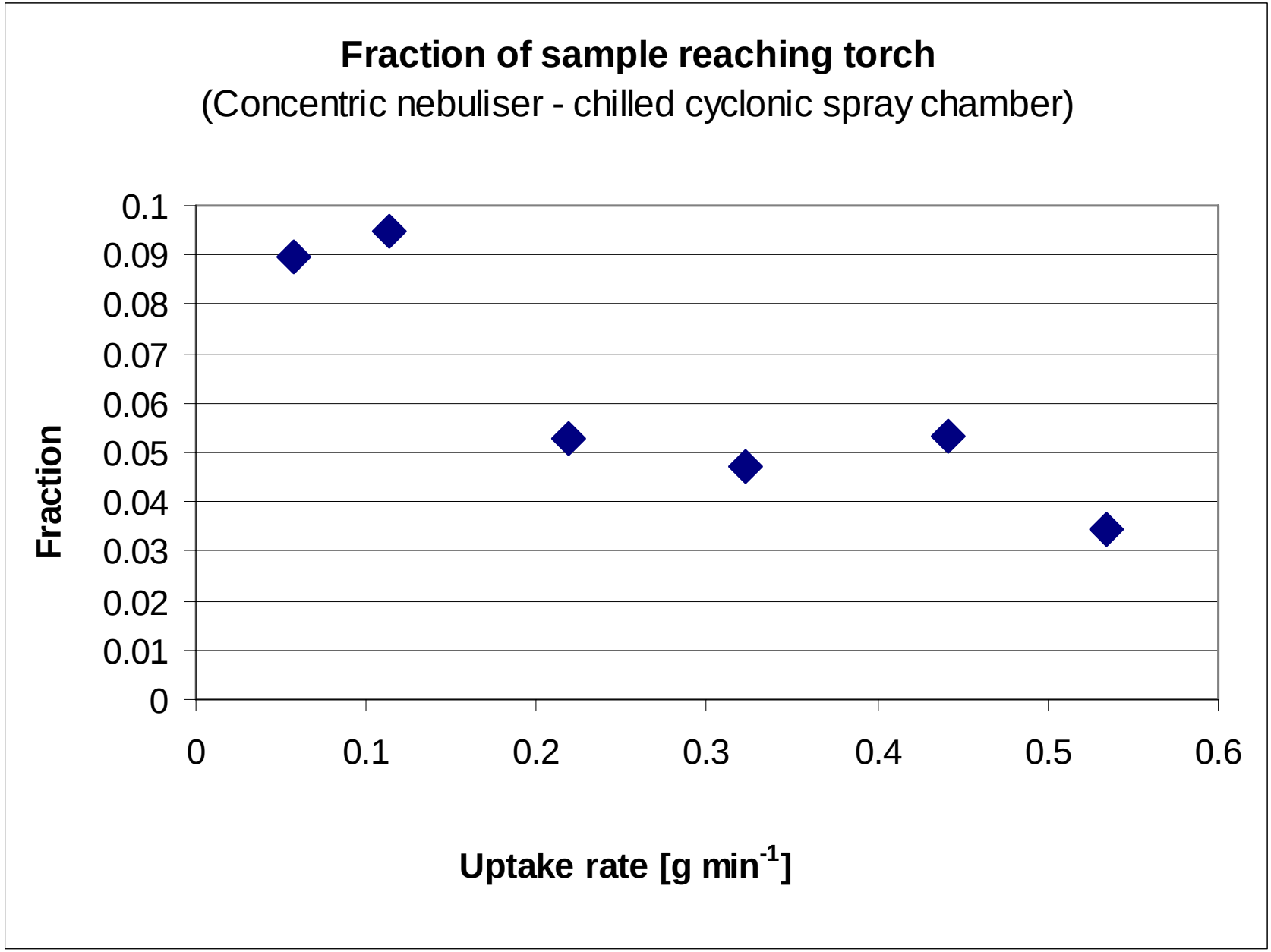
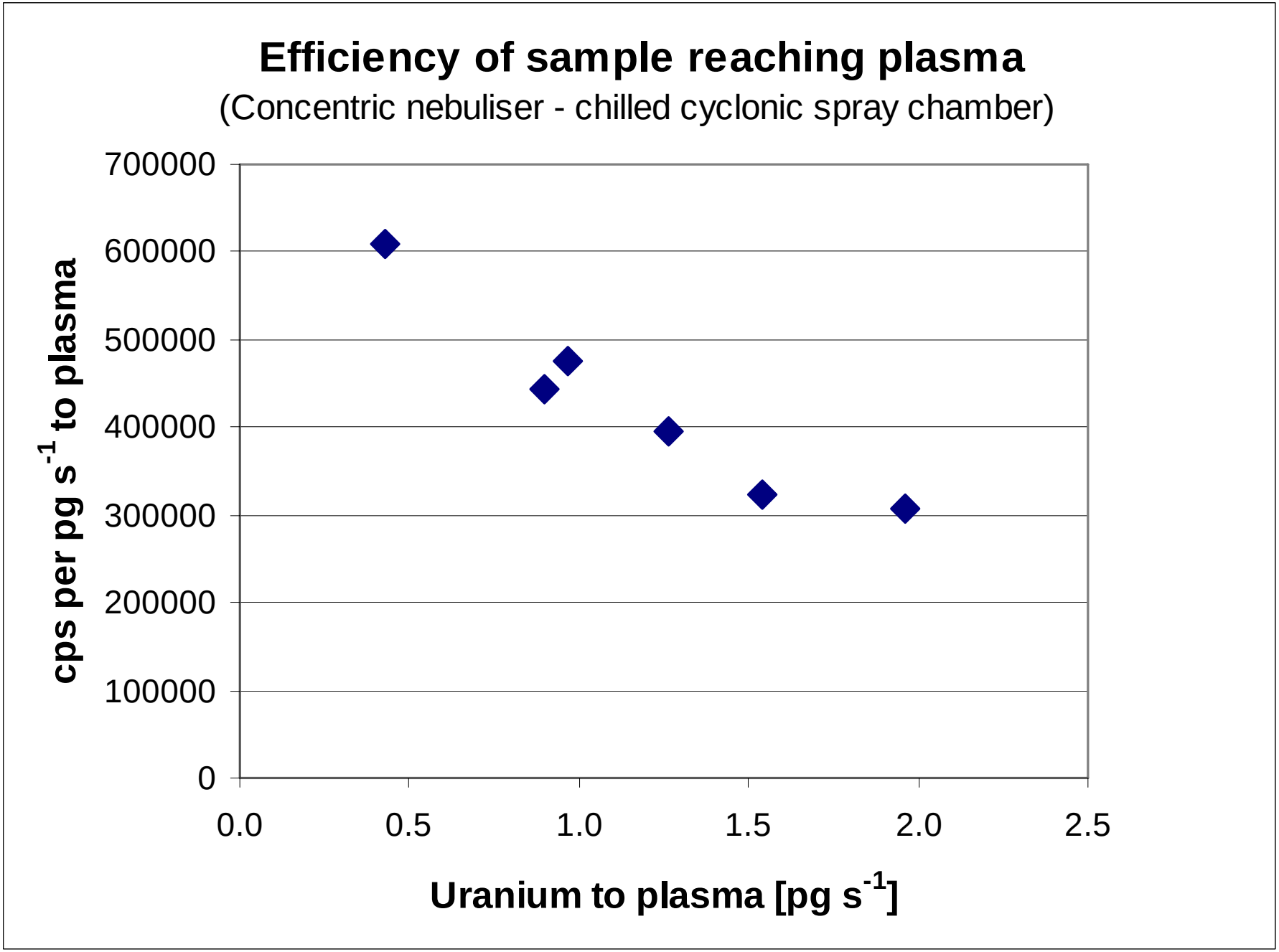


Figure 3.22 Schematic diagram of the DIHEN interfaced with a demountable plasma torch. (Revised from Reference 269, with permission.)

Best use of a limited amount of sample




Fraction of sample reaching torch
(Concentric nebuliser - chilled cyclonic spray chamber)
Fraction
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.1
0.2
0.3
0.4
0.5
0.6
Uptake rate [g min-1]


Efficiency of sample reaching plasma
(Concentric nebuliser - chilled cyclonic spray chamber)
cps per pg s-1 to plasma
700000
600000
500000
400000
300000
200000
100000
0
0.0
0.5
1.0
1.5
2.0
2.5
Uranium to plasma [pg s-1]

Isotope ratio measurements

- Mass discrimanation
- Dead time corrections
- Reference materials !

Table 2
Precision and accuracy of DIHEN-ICP-SFMS measuring uranium isotope standard solutions NIST U005, U350, U930 and U(nat) (U_{conc} = 0.1 ppb, n = 6)

	Isotope ratios		Precision (R.S.D., %)	Accuracy (%)
	Measured	Certified		
U005				
$^{235}U/^{238}U$	0.0049435	0.0049194	1.4	0.5
$^{234}U/^{238}U$	0.0000218	0.0000219	1.8	−0.12
$^{236}U/^{238}U$	0.0000472	0.0000468	4.3	0.9
U350				
$^{235}U/^{238}U$	0.540114	0.546488	1.6	−1.2
$^{234}U/^{238}U$	0.003863	0.003879	3.2	−0.41
$^{236}U/^{238}U$	0.002644	0.002598	1.3	1.8
U930				
$^{235}U/^{238}U$	17.3472	17.3487	2.0	−0.01
$^{234}U/^{238}U$	0.2005	0.2010	1.9	−0.23
$^{236}U/^{238}U$	0.03783	0.03768	2.8	0.4
U(nat)				
$^{235}U/^{238}U$	0.007227	0.007253	1.1	−0.3
$^{234}U/^{238}U$	0.000054	0.000055	0.1	−0.52

Problems in isotope ratio measurements (single collectors)

- Sample introduction system
- Plasma instability
- Dead time corrections
- Mass fractionation
- Interferences
- Abundance sensitivity (peak tailing)

Mass discrimination at interface

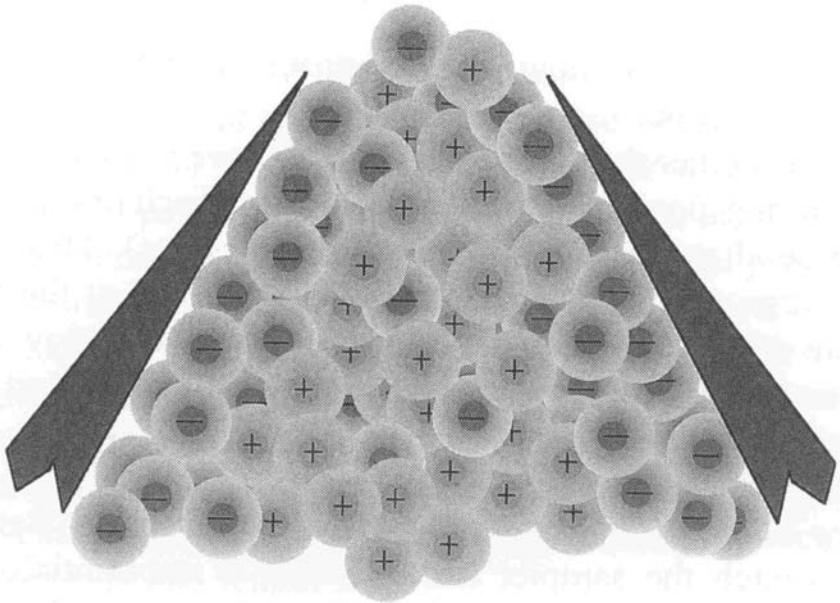


Plate 2 Under high charge density conditions, the Debye spheres of the charged particles overlap and the particles experience modified fields (they are "shielded" from the applied electrostatic field). Because of their higher mobility, electrons preferentially diffuse to the walls where an electron sheath forms. Due to the electron diffusion, a net positive charge density remains on axis and the resultant space charge field is positive. See color plate.

Mass discrimination

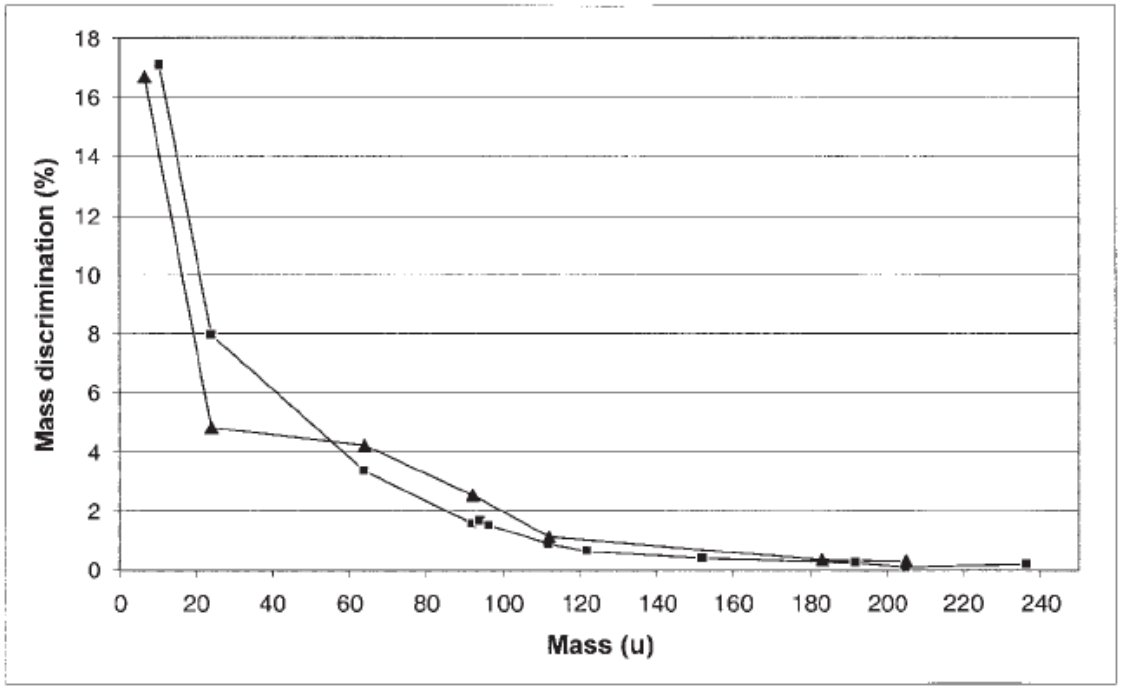


Fig. 2 Mass discrimination per mass unit in ICP-QMS. —■— Platform ICP-MS; —▲— Elan 5000 [1] (rf power 1350 W, nebulizer gas 0.86 L min^{-1}; collision gas: He – 4 ml min^{-1}; H_2 – 1.5 min min^{-1}, hexapole bias 0 V)[1]

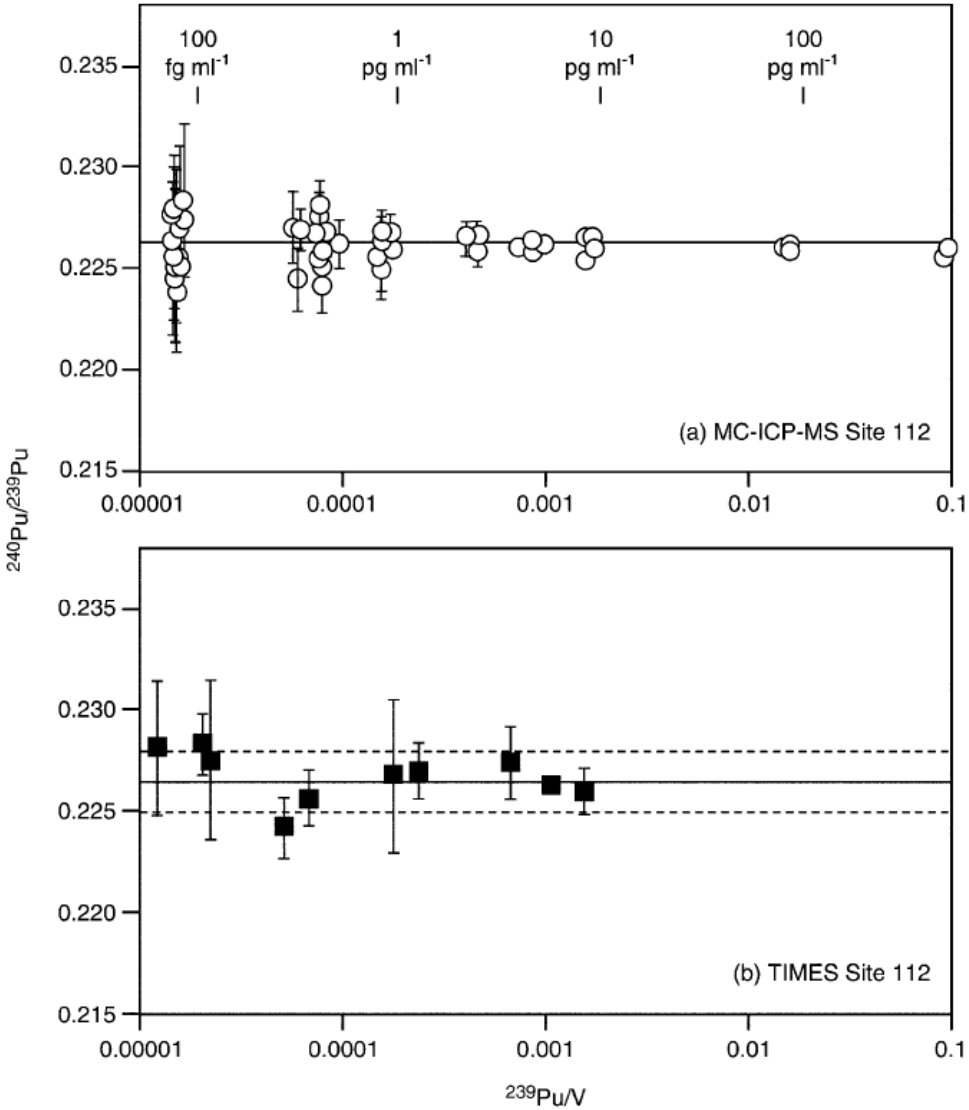


Fig. 5. Plutonium isotope ratio analysis at femtogram to nanogram levels by MC-ICP-CC-MS vs. TIMS (from Ref. [9] with permission).

Table 2 Isotope ratio measurements by different ICP-MS methods

Isotope ratio	Method	Precision	Sample size	Reference
$^{235}U/^{238}U$~1	ICP-QMS	0.028%[a]	255 pg	Platzner et al. [24]
$^{207}Pb/^{206}Pb$~0.9	DRC-ICP-QMS	0.057% 0.027%[a]	440 ng 5.1 µg	Bandura and Tanner [44]
$^{235}U/^{238}U$~1	DF-ICP-MS	0.026% 0.2%	255 pg 0.5 pg	Becker and Dietze [28]
$^{34}S/^{32}S$~0.05	Hex-ICP-QMS	0.03%	50–250 µg	Mason et al. [40]
$^{137}Ba/^{138}Ba$	TOF-ICP-QMS	0.05%	250 ng	Vanhaecke et al. [34]
$^{208}Pb/^{206}Pb$	MC-ICP-MS	0.006%	100 mg	Rehkämper and Halliday [52]
$^{182}W/^{183}W$~2	MC-ICP-MS	0.006%	0.5–1 µg	Lee and Halliday [50]
$^{63}Cu/^{65}Cu$	MC-ICP-MS	0.002%	100 ng	Maréchal et al. [54]

[a] long term precision

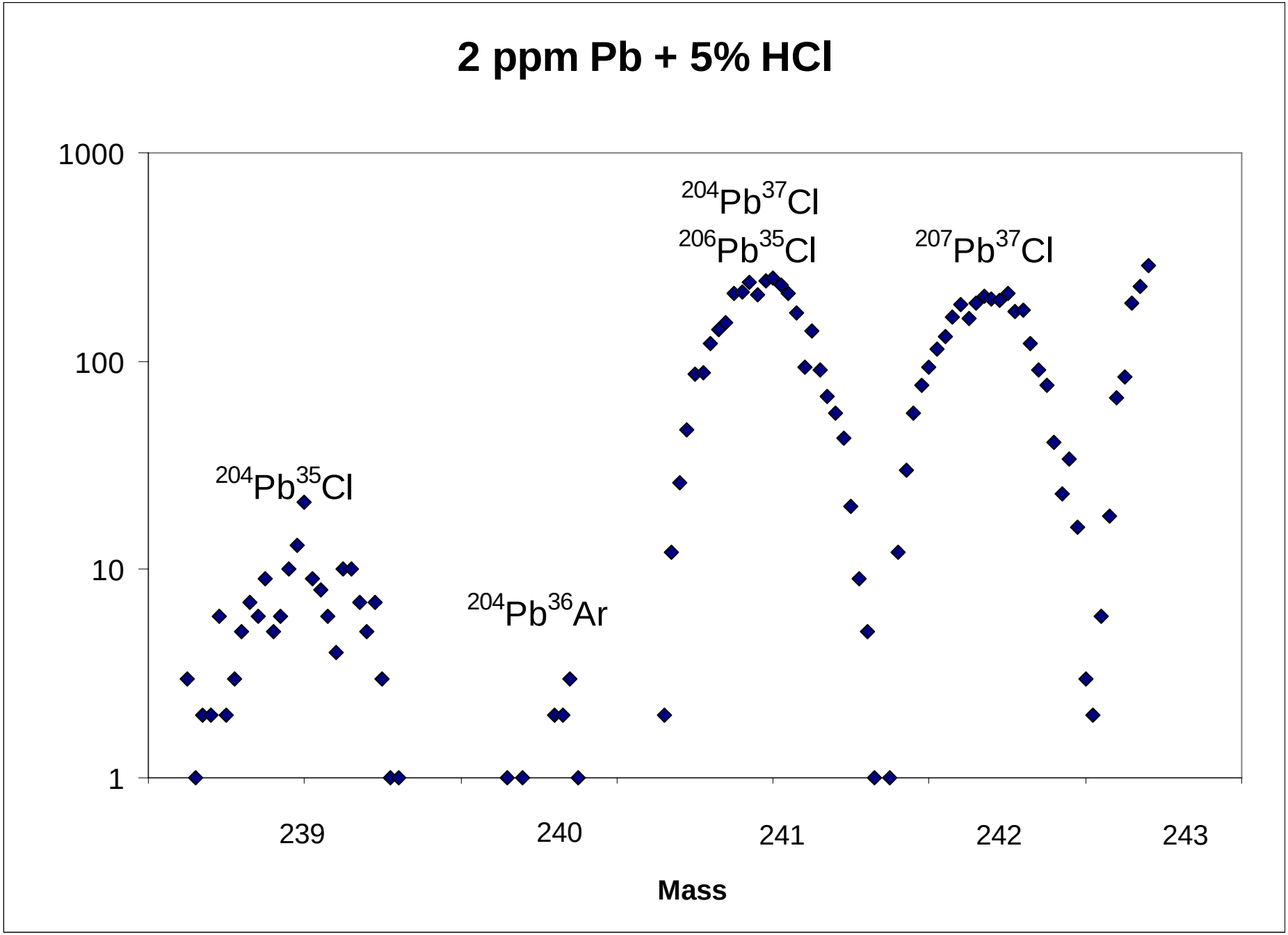
Different separation chemistry relative to ”alpha spectrometry”

Table 1
Possible interferences for Pu isotopes and required mass resolution on ICP-SFMS

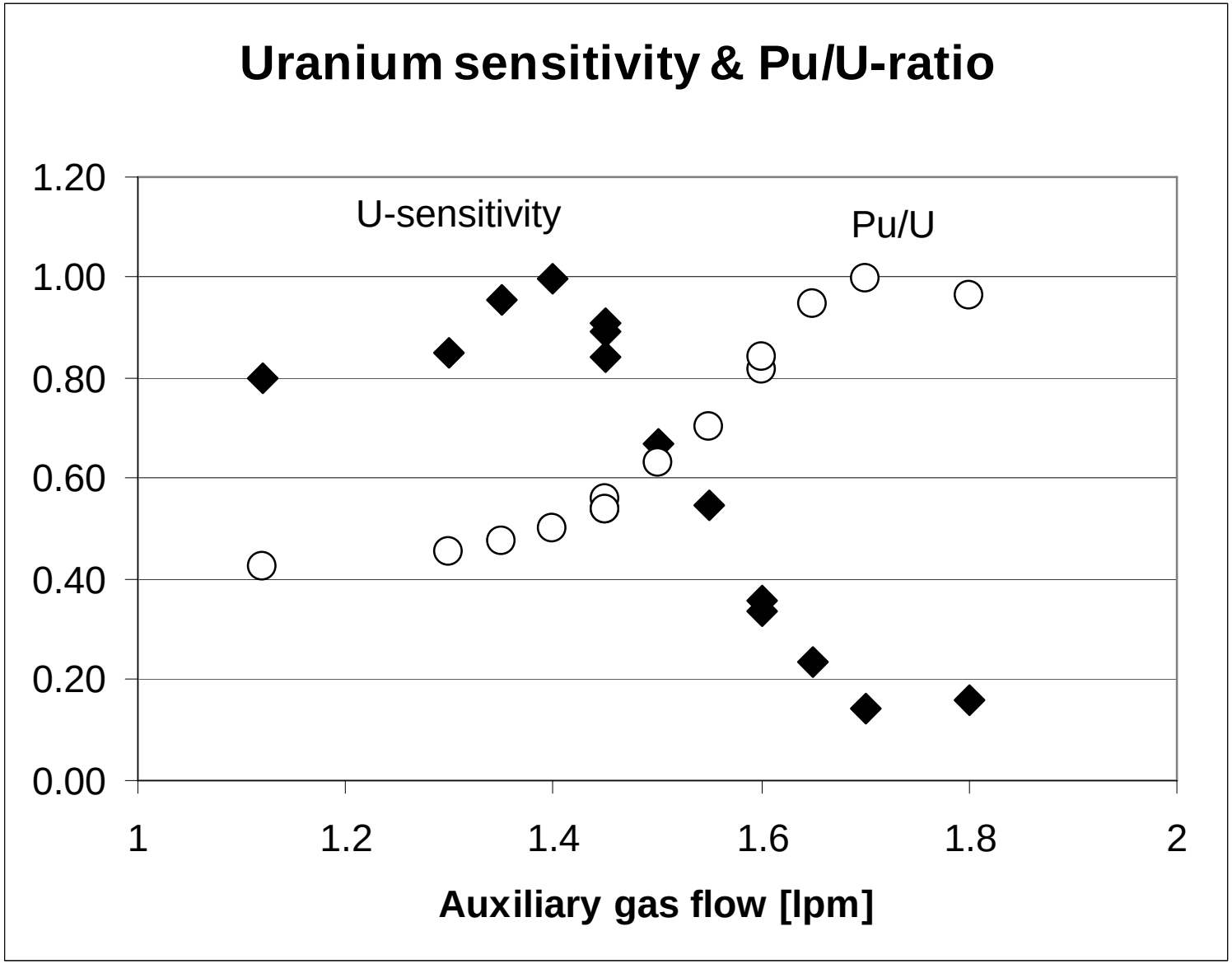
Nuclide	Molecular ions	Required mass resolution, $m/\Delta m$
^{238}Pu	$^{238}U^{+}$	193665
	$^{206}Pb^{16}O^{14}N^{1}H_2^{+}$	3874
	$^{208}Pb^{16}O^{1}H_2{}^{12}C^{+}$	3818
	$^{208}Pb^{14}N_2{}^{1}H_2^{+}$	4654
^{239}Pu	$^{238}U^{1}H^{+}$	36885
	$^{207}Pb^{16}O^{14}N^{1}H_2^{+}$	3817
	$^{208}Pb^{16}O^{14}N^{1}H^{+}$	3430
^{240}Pu	$^{238}U^{1}H_2^{+}$	19116
	$^{208}Pb^{16}O^{14}N^{1}H_2^{+}$	3774
^{241}Pu	$^{207}Pb^{16}O_2{}^{1}H_2^{+}$	3193
^{242}Pu	$^{208}Pb^{16}O_2{}^{1}H_2^{+}$	3159
^{244}Pu	$^{206}Pb^{12}C_3{}^{1}H_2^{+}$	3293
	$^{207}Pb^{12}O_3{}^{1}H^{+}$	3031

Table 1
Possible interferences for ^{90}Sr and Pu isotopes and required mass resolution on ICP-SFMS

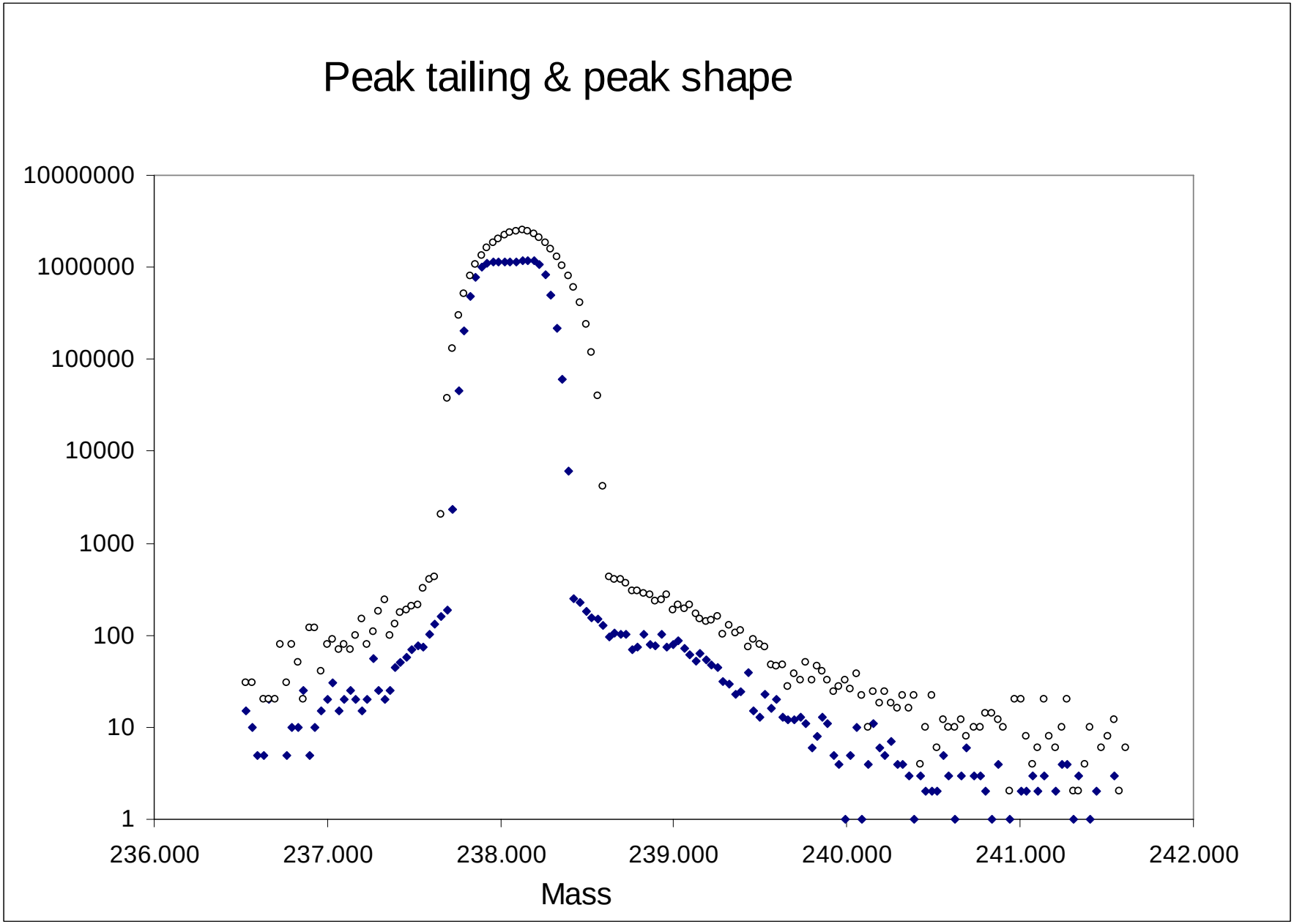
Nuclide	Molecular ions	Required mass resolution ($m/\Delta m$)
^{90}Sr	$^{180}W^{2+}$	1370
	$^{180}Hf^{2+}$	1372
	$^{58}Ni^{16}O_2{}^{+}$	2315
	$^{74}Ge^{16}O^{+}$	10765
	$^{52}Cr^{38}Ar^{+}$	19987
	$^{50}V^{40}Ar^{+}$	49894
	$^{54}Fe^{36}Ar^{+}$	155548
	$^{50}Ti^{40}Ar^{+}$	158287
	$^{90}Zr^{+}$	29877
^{239}Pu	$^{238}U^{1}H^{+}$	36885
	$^{207}Pb^{16}O^{14}N^{1}H_2{}^{+}$	3817
	$^{208}Pb^{16}O^{14}N^{1}H^{+}$	3430
^{240}Pu	$^{238}U^{1}H_2{}^{+}$	19116
	$^{208}Pb^{16}O^{14}N^{1}H_2{}^{+}$	3774

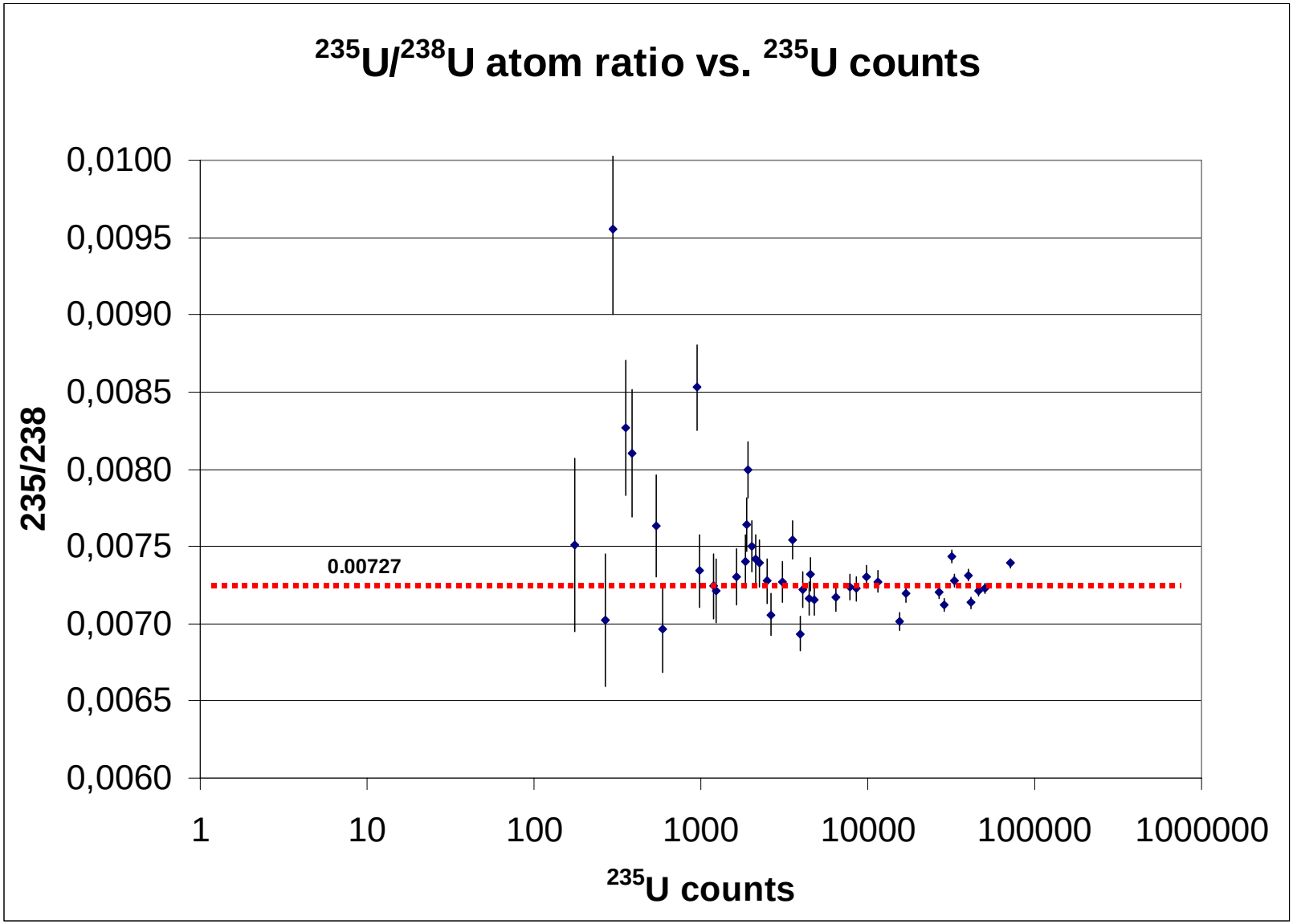

2 ppm Pb + 5% HCl
1000
100
10
1
$^{204}Pb^{35}Cl$
$^{204}Pb^{36}Ar$
$^{204}Pb^{37}Cl$
$^{206}Pb^{35}Cl$
$^{207}Pb^{37}Cl$
239
240
241
242
243
Mass

Tuning for Pu-analysis – we use uranium

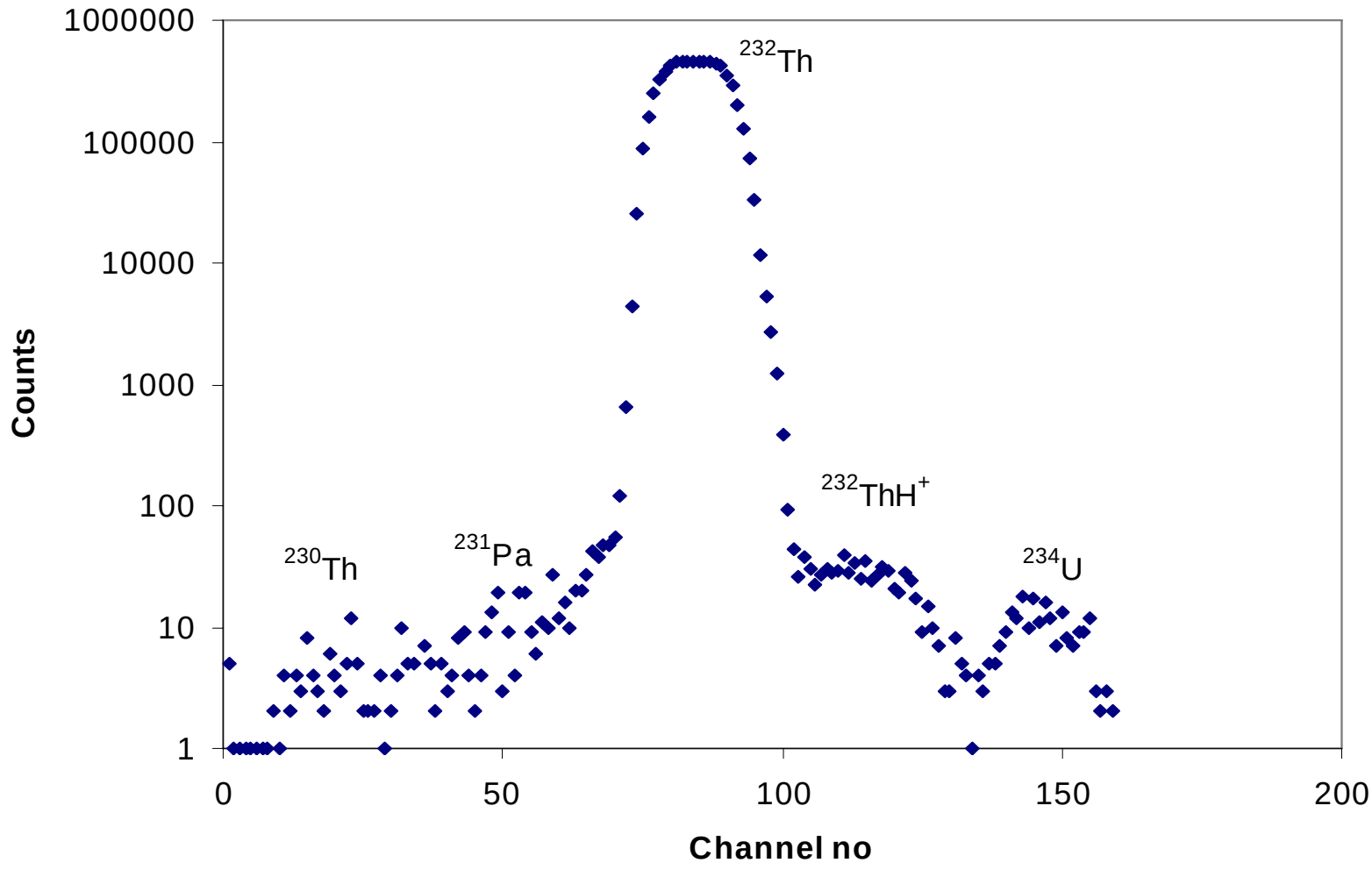


The need to remove uranium in Pu-analysis

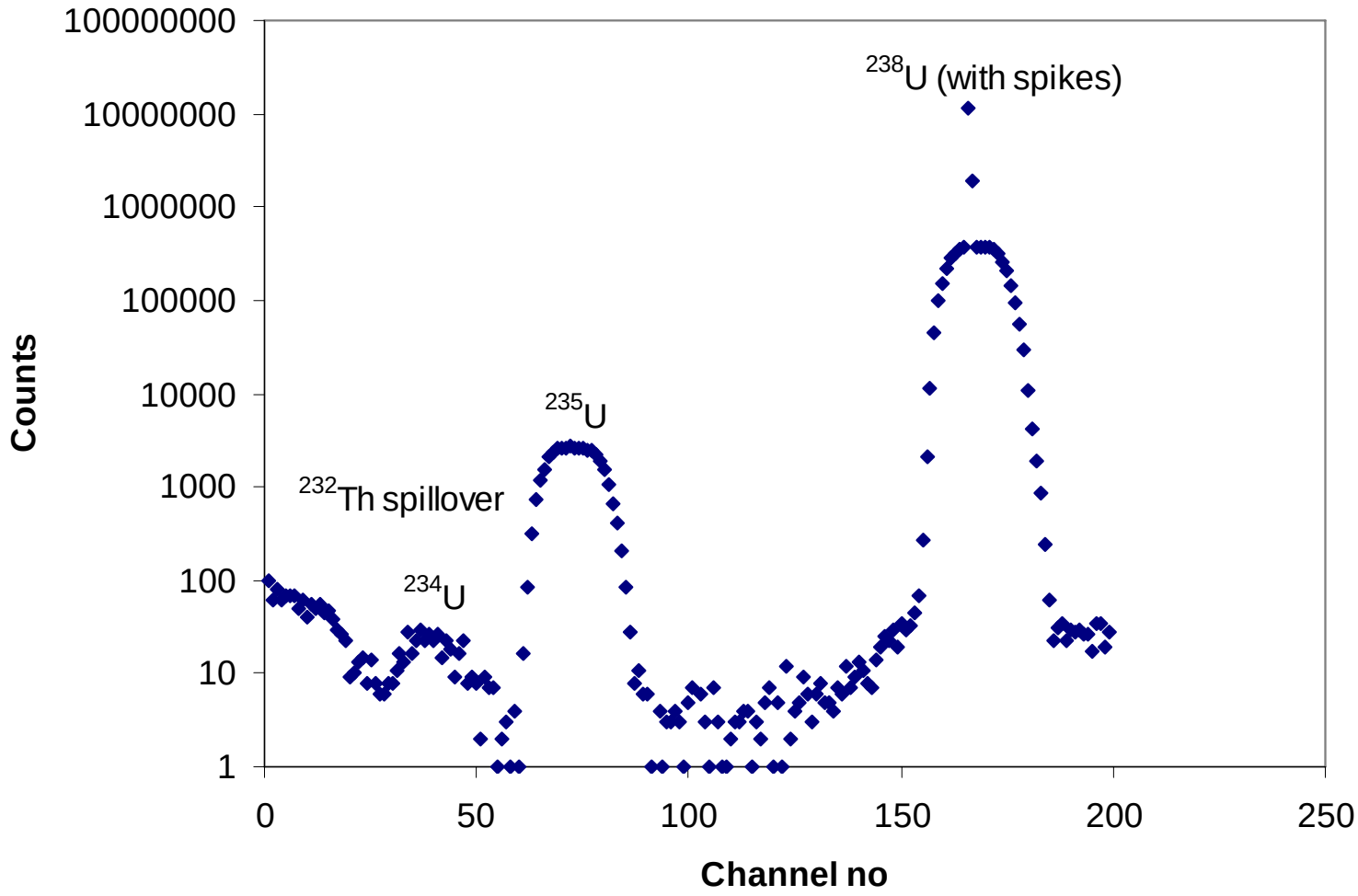


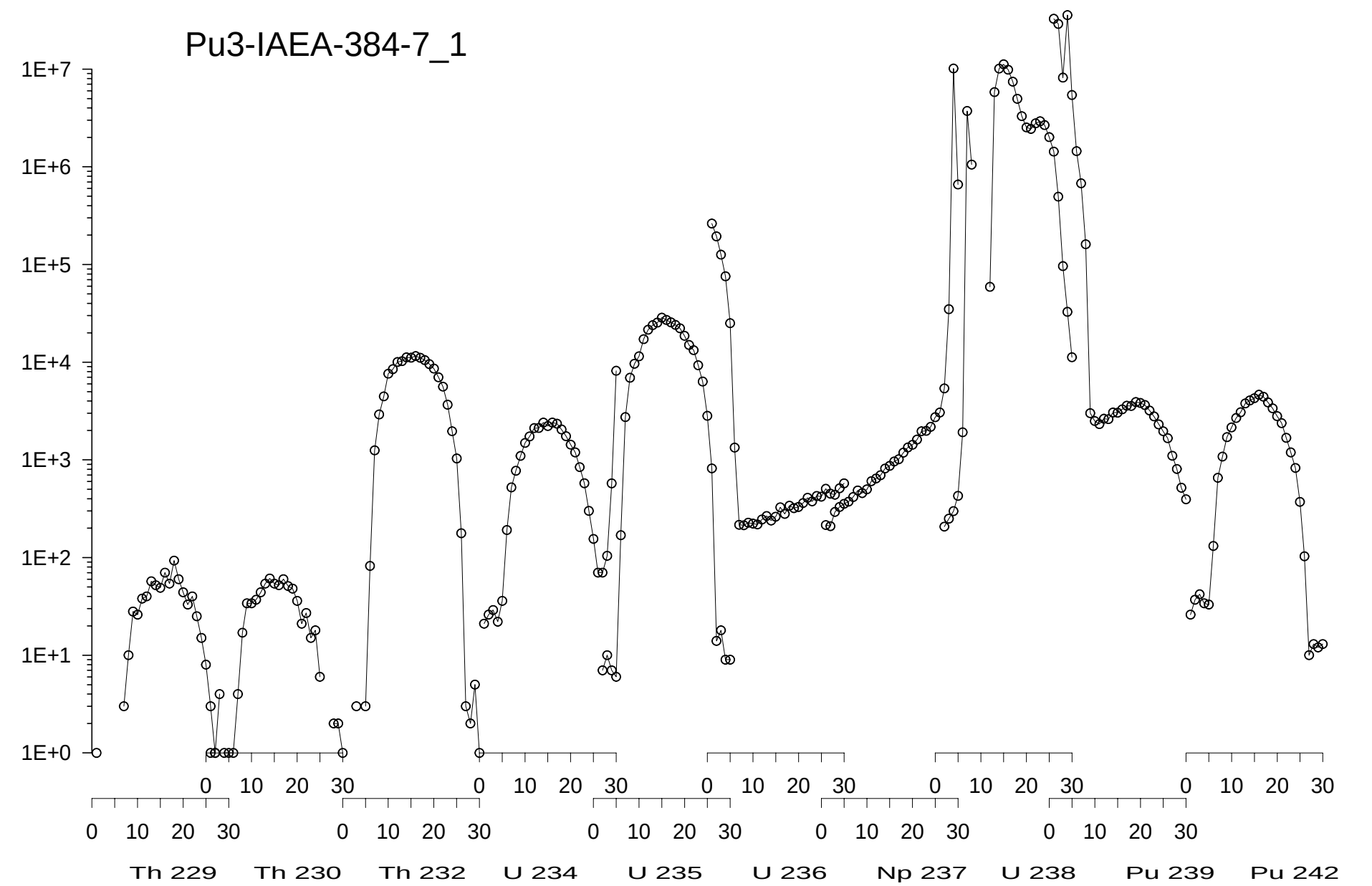

235U/238U atom ratio vs. 235U counts
0,0100
0,0095
0,0090
0,0085
0,0080
0,0075
0,0070
0,0065
0,0060
235/238
0.00727
1
10
100
1000
10000
100000
1000000
235U counts

Abundance sensitivity thorium, natural soil sample without radiochemistry

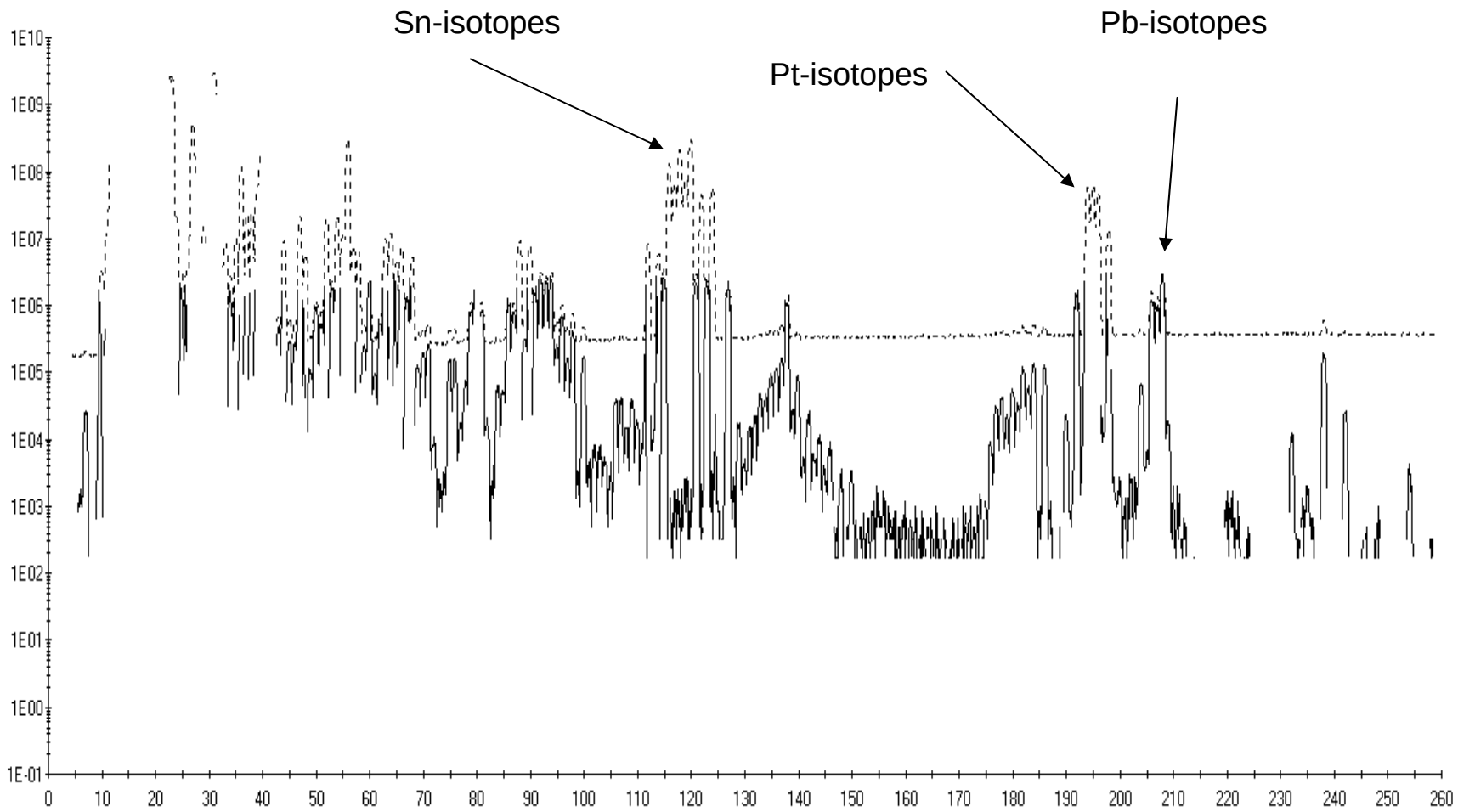


Abundance sensitivity natural uranium in soil. No radiochemistry



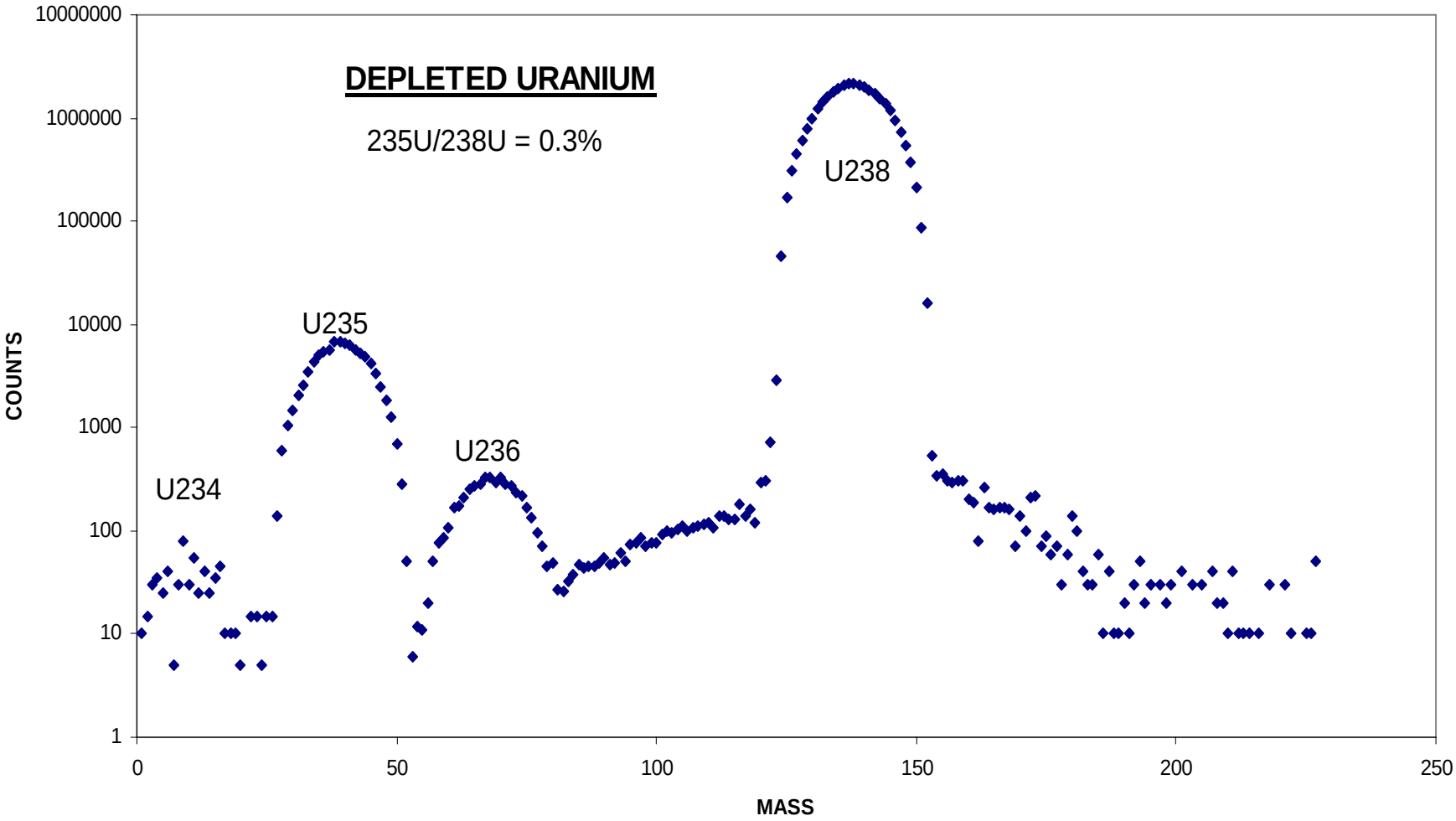

Pu3-IAEA-384-7_1
1E+7
1E+6
1E+5
1E+4
1E+3
1E+2
1E+1
1E+0
0 10 20 30
Th 229
Th 230
Th 232
U 234
U 235
U 236
Np 237
U 238
Pu 239
Pu 242

Polyatomic inteferences – Pu analysis (stripped steel disc)

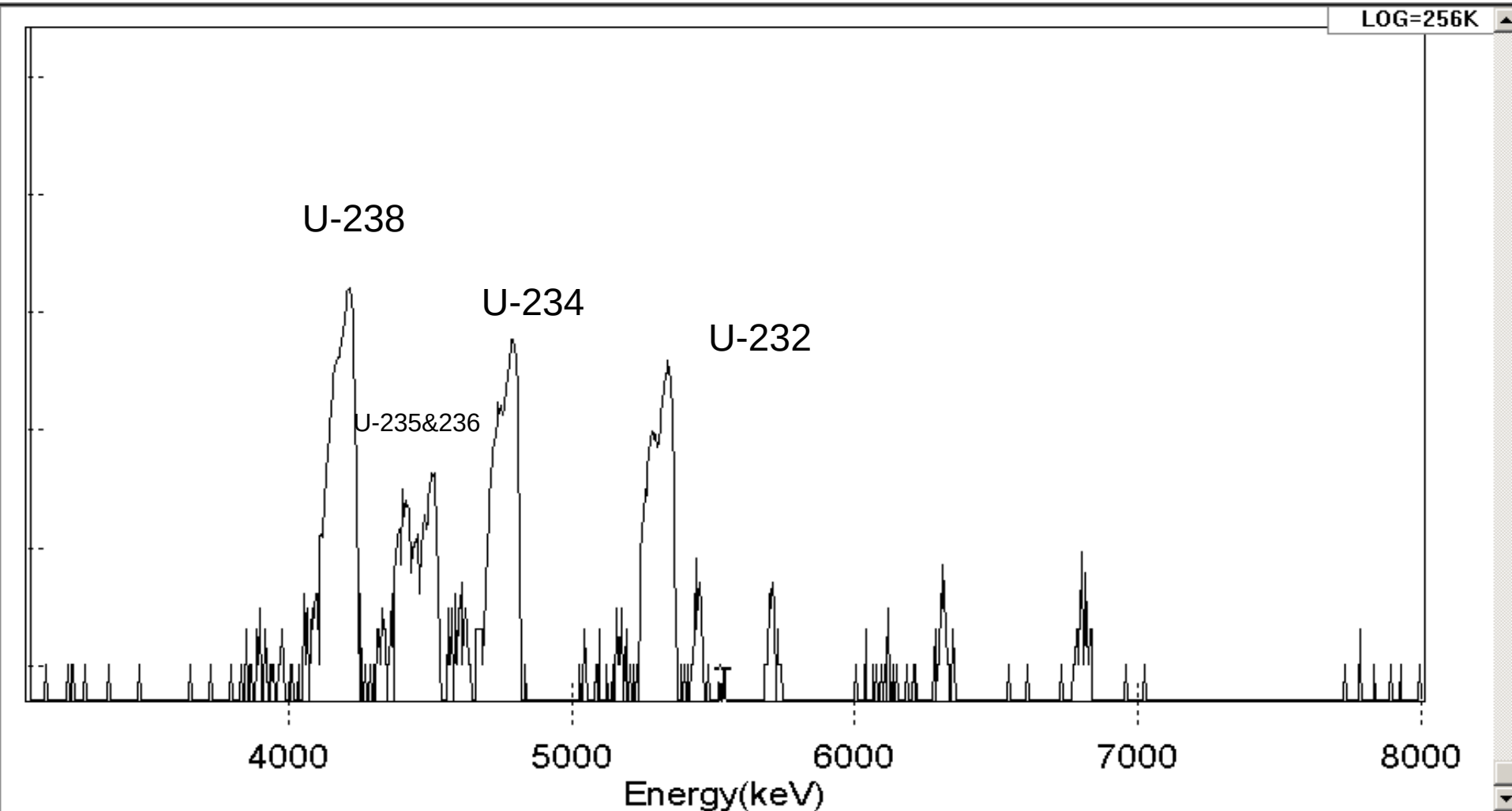


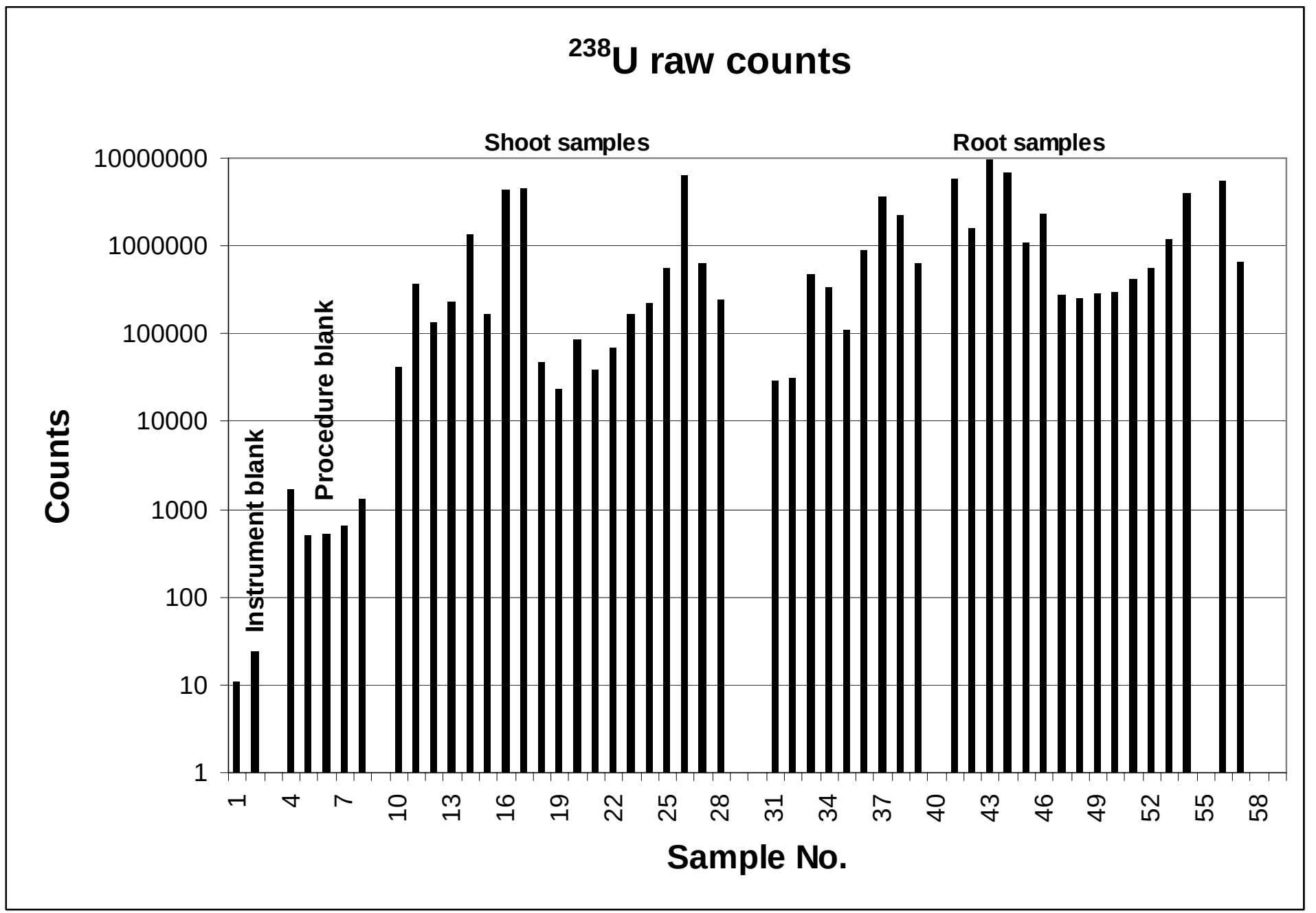
Uranium isotopes

- ^{238}U, ^{235}U, ^{234}U as natural U-isotopes.
- ^{236}U (^{233}U) as artificial U-isotopes.
- Complicated isotope signature in recycled uranium require MS.

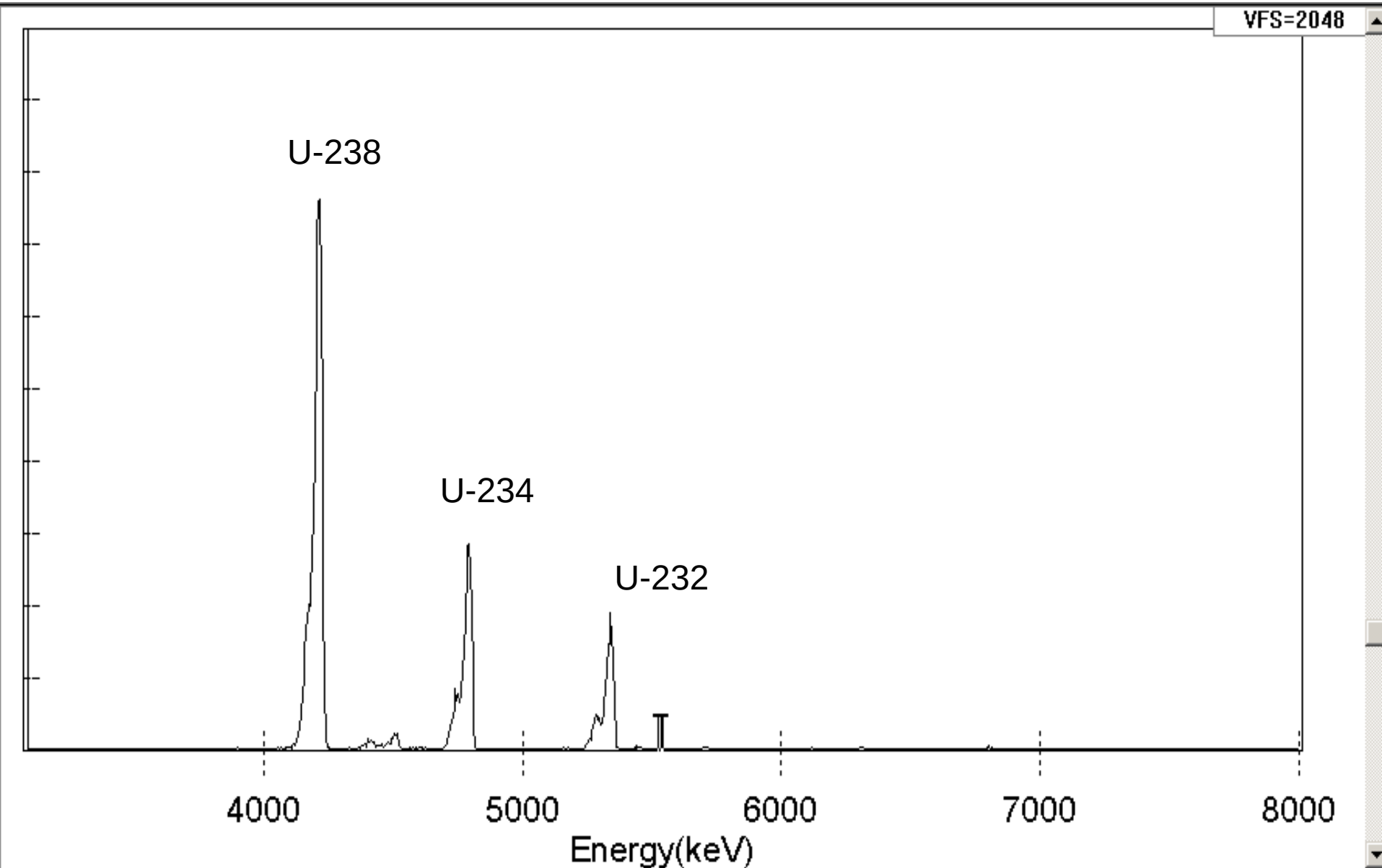

DEPLETED URANIUM
235U/238U = 0.3%
U234
U235
U236
U238
COUNTS
MASS
10000000
1000000
100000
10000
1000
100
10
1
0
50
100
150
200
250

Depleted and recycled uranium

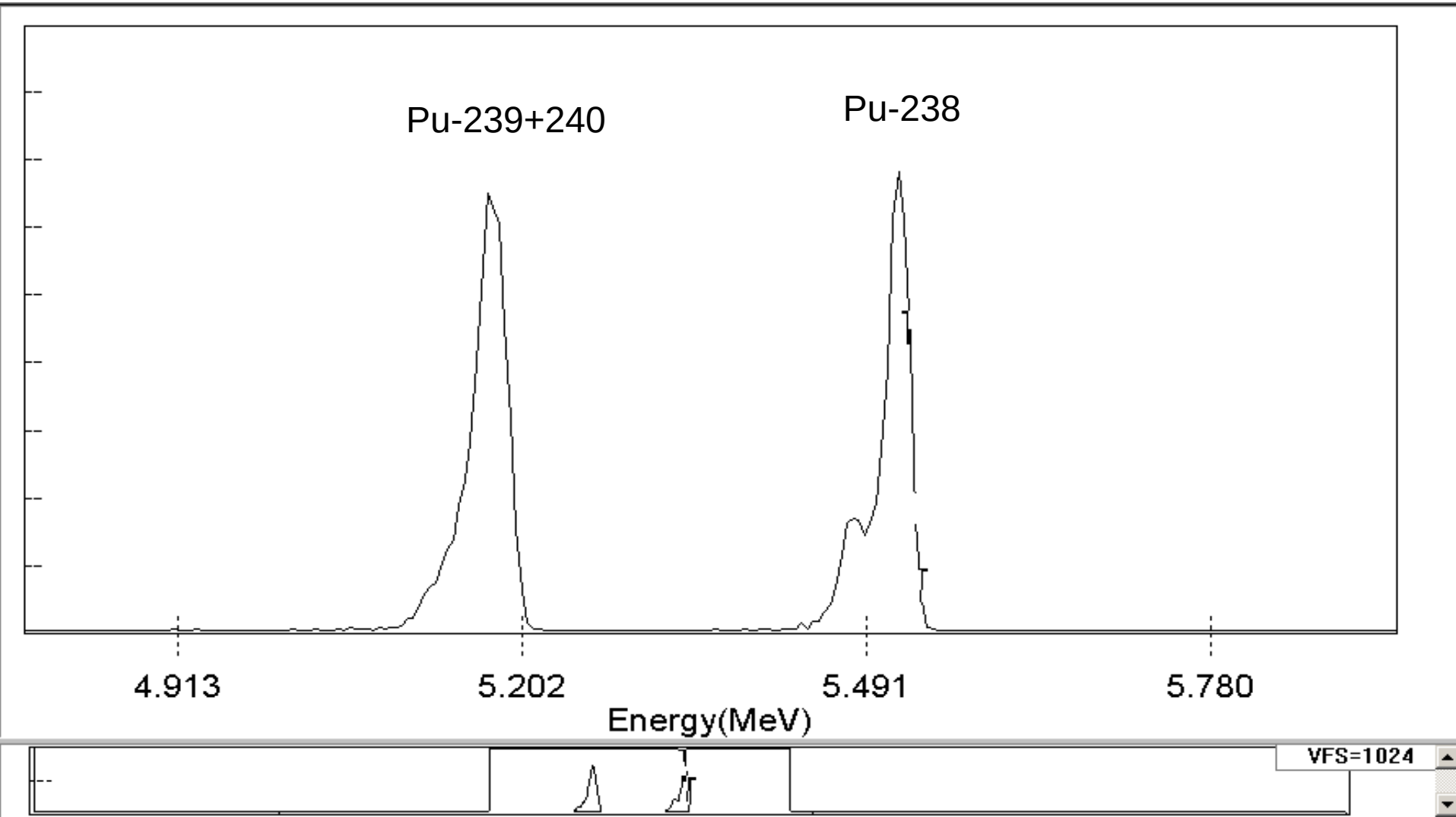



238U raw counts
Shoot samples
Root samples
Instrument blank
Procedure blank
Counts
10000000
1000000
100000
10000
1000
100
10
1
1
4
7
10
13
16
19
22
25
28
31
34
37
40
43
46
49
52
55
58
Sample No.

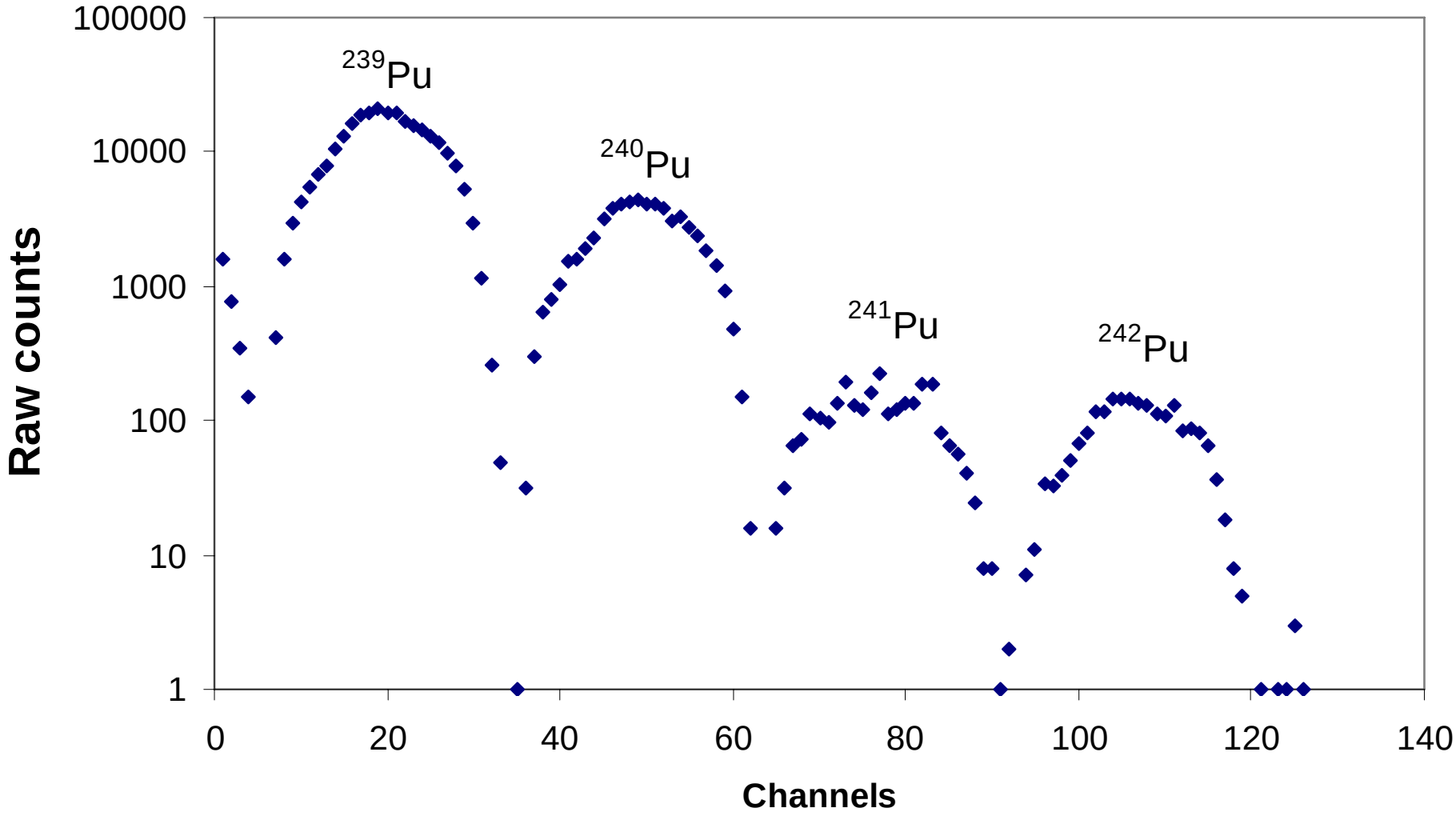
Depleted and recycled uranium – alpha spectrometry



Pu without tracer – alpha spectrometry



Pu-isotopes Irish Sea Sediments - ICP-MS



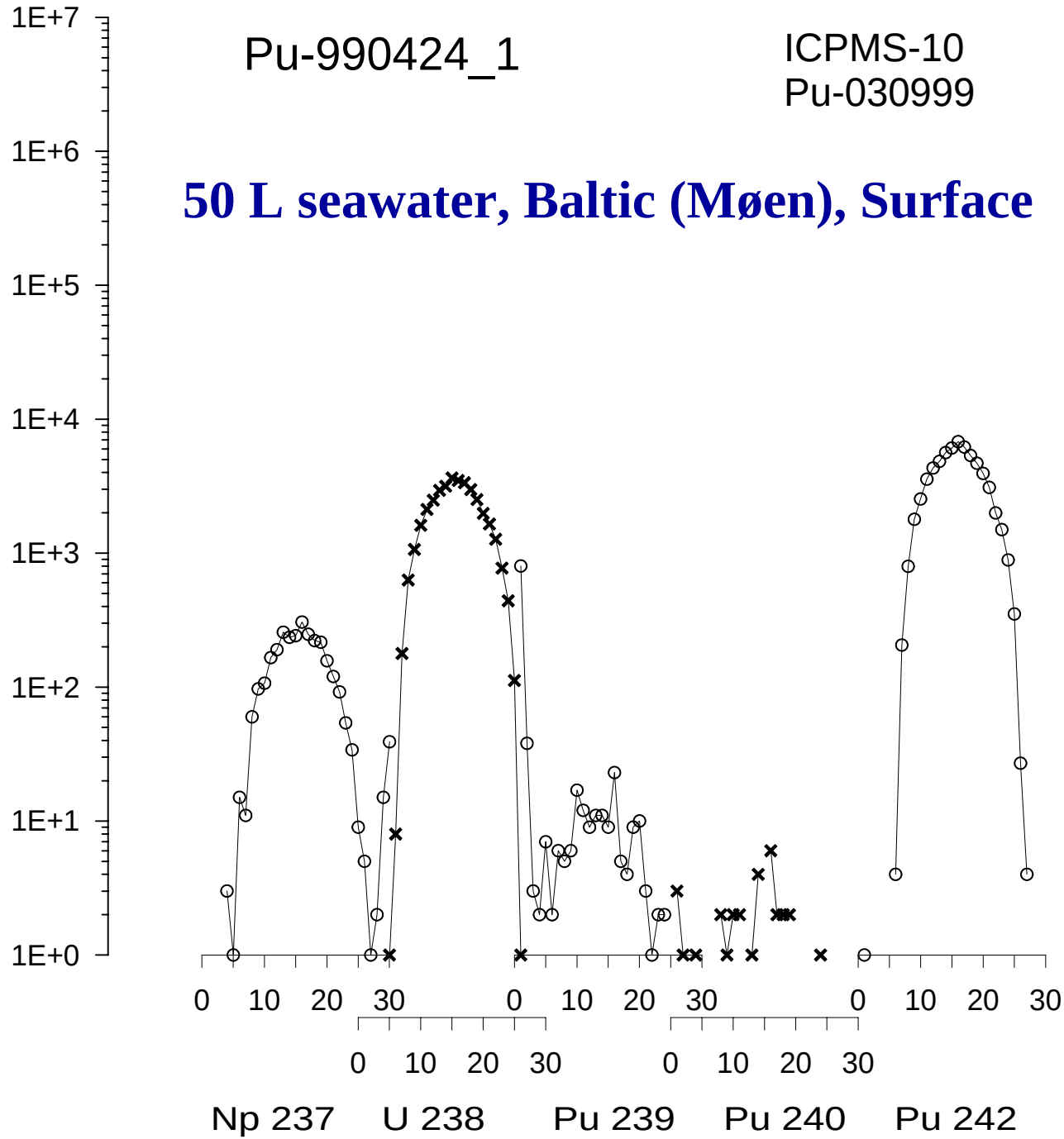

Pu-990424_1
ICPMS-10
Pu-030999
50 L seawater, Baltic (Møen), Surface
1E+7
1E+6
1E+5
1E+4
1E+3
1E+2
1E+1
1E+0
0 10 20 30
Np 237
U 238
Pu 239
Pu 240
Pu 242

Table 7
Characteristics of different ICP-MS instruments using microcentric nebulizer with desolvator (Aridus, Cetac Technologies)

	Absolute sensitivity (counts/atom)	UH^+/U^+	Abundance sensitivity
ICP-QMS[a]	4×10^{-5}	3×10^{-6}	6×10^{-7}
ICP-SFMS	7×10^{-4}	3×10^{-5}	5×10^{-6}
MC-ICP-MS[b]	5×10^{-4}	5×10^{-5}	3×10^{-7}

[a] ELAN 6000.
[b] Halicz [94].

Determinations of $^{240}Pu/^{239}Pu$ atom ratio in Normass reference soil

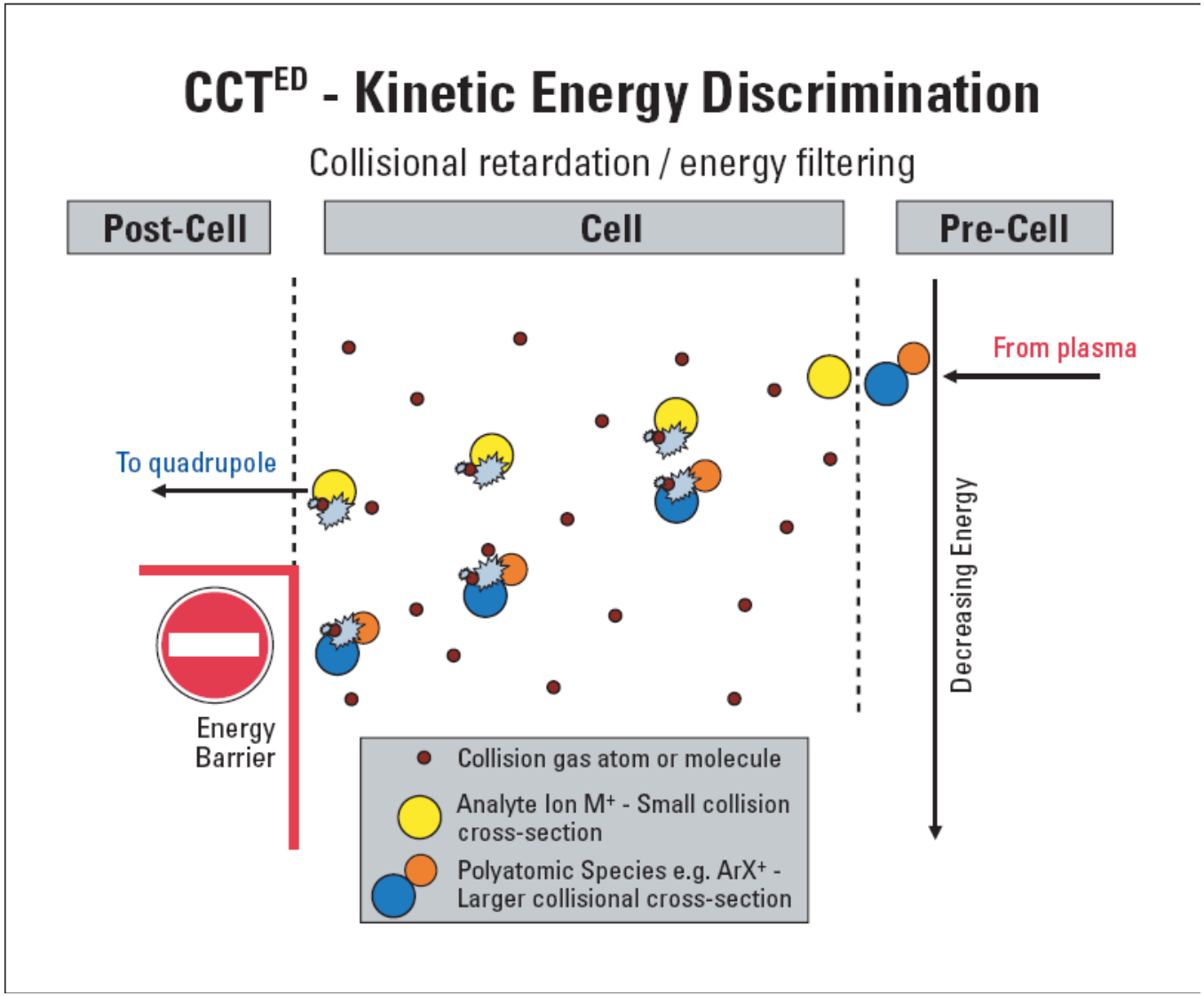
(Leached soil solution)

	$^{240}Pu/^{239}Pu$
Lab 1	0.187 ± 0.004
Lab 2	0.193 ± 0.004
Lab 3	0.187 ± 0.006
Kelley et.al. 'Roskilde soil' (Sci.Tot. Env. 237/238, 1999, 483-500)	0.1904 ± 0.0012

Run No.	Atom $^{240}Pu/^{239}Pu$	Atom $^{237}Np/^{239}Pu$	$^{239+240}Pu$ mBq/g ICP	$^{239+240}Pu$ mBq/g alfa
Soil-1	0.1908	0.283	0.240	0.251
Soil-2	0.1818	0.362	0.246	0.239
Soil-3	0.1969	0.329	0.239	0.238
Soil-4	0.1965	0.318	0.238	0.235
Soil-5	0.1895	0.294	0.227	0.231
Soil-6	0.1887	0.304	0.239	0.238
Soil-7	0.1928	0.316	0.240	0.246
Soil-8	0.1790	0.371	0.240	0.233
			0.238±0.0018	0.238±0.0087
Atom ratio:	0.1895±0.0023	0.322±0.01		
Roskilde (Kelley et.al.)	0.1904±0.0012	0.531±0.013		

Run No.	^{238}U	^{239}Pu	^{240}Pu	Atom $^{240}Pu/^{239}Pu$
1	1223	5000	911	0.1822
2	1180	5310	990	0.1864
3	1143	5368	923	0.1719
4	1082	5196	955	0.1838
5	1135	5111	964	0.1886
6	1058	5185	957	0.1846
7	1069	5140	979	0.1905
8	1117	5174	938	0.1813
9	980	4937	975	0.1975
10	1081	5004	967	0.1932
11	1031	5013	959	0.1913
12	991	5080	968	0.1906
13	1012	4985	894	0.1793
14	958	5179	966	0.1865
15	1020	4899	948	0.1935
Atom ratio:				0.1868±0.0065 (1 std.dev)

Collision- and reaction cells



Collision cell and I-129 analysis

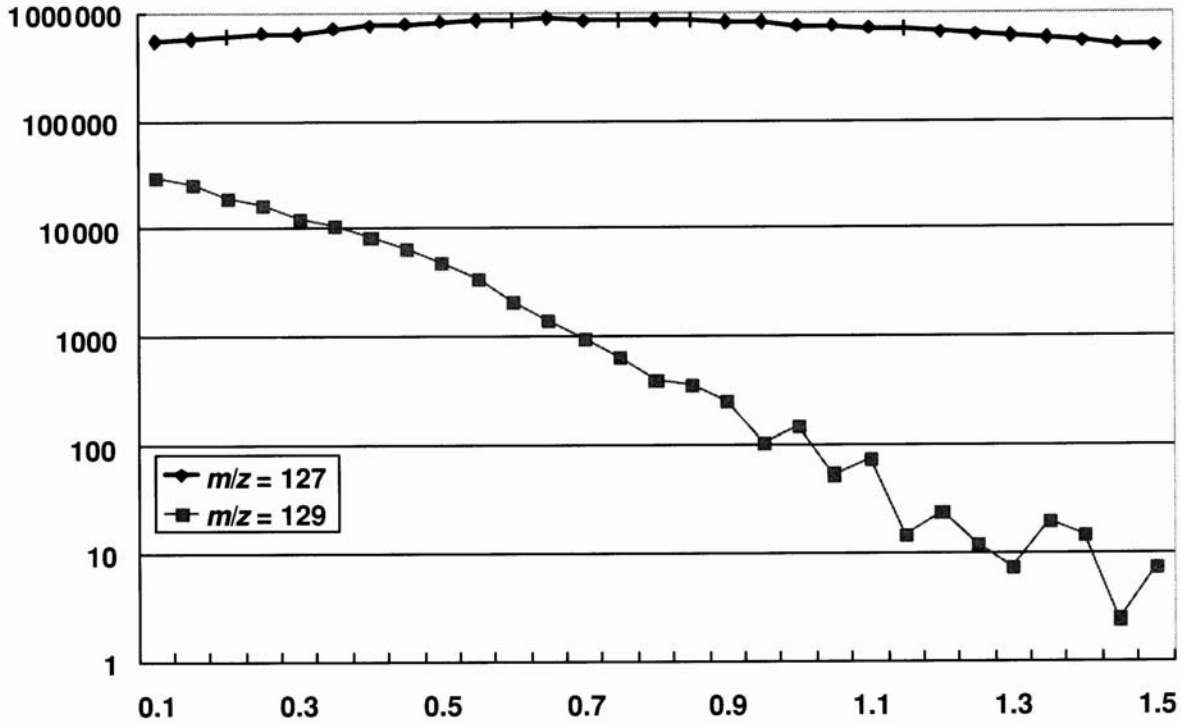
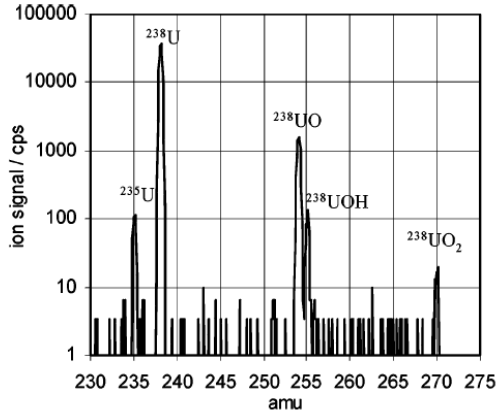
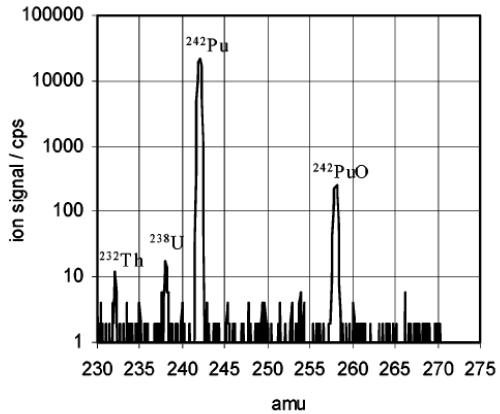


Figure 9.15 Cell gas optimisation for ^{129}Xe background.





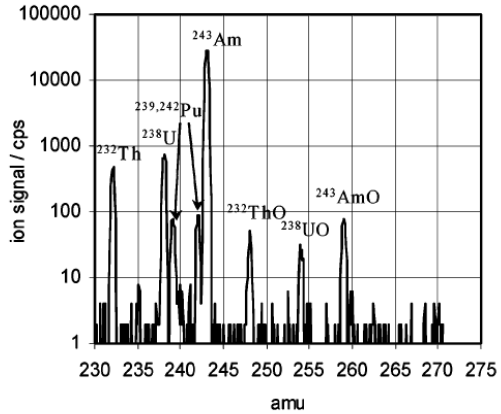
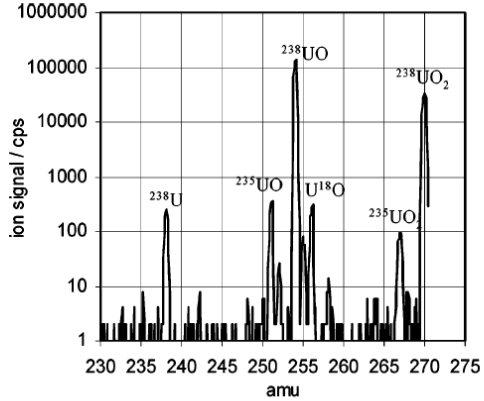
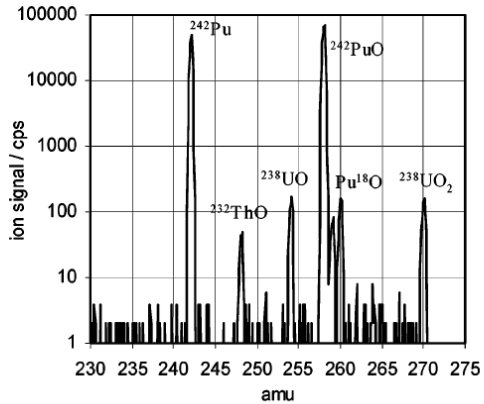


Figure 1. Mass spectra for samples containing 1 ppb single-element standards of U, Pu, and Am (see text for impurities in Am sample), in standard mode without reaction gas.





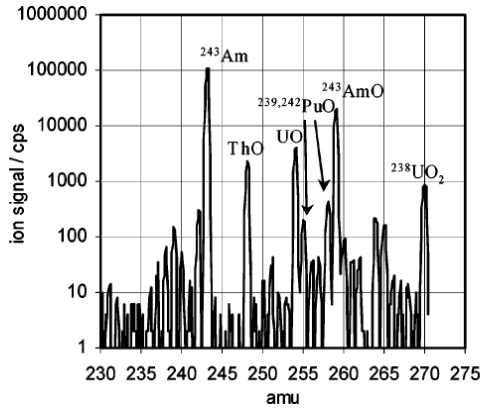


Figure 3. Mass spectra for samples containing 1 ppb single-element standards of U, Pu, and Am with carbon dioxide gas (0.5 Ar-equivalent sccm, 0.25 true sccm).